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A Review of Rate Constants of Selected Reactions of Interest in Re-Entry Flow Fields in the Atmosphere

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A Review of Rate Constants of Selected Reactions of Interest in Re-Entry Flow Fields in the Atmosphere

M. H. Bortner

Office of Standard Reference Data
National Bureau of Standards
Washington, D.C. 20234

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A Review of Rate Constants of Selected Reactions of Interest in Re-Entry Flow Fields in the Atmosphere[1]

M. H. Bortner

The major reactions normally encountered in flow field re-entry calculations for the oxygen nitrogen system are reviewed and a rate constant value for each reaction is recommended. Collisional ionization processes, charge exchange reactions and attachment-detachment reactions are included. Rate constant coefficients to fit the equation $k = aT^b e^{-c/T}$ are reported in tabular form for the selected rate constant. The data are also graphed as log k vs T(K). In all, over twenty forward and reverse reactions are reviewed. Additionally, a large number of rate constant values for reactions which also effect flow field calculations are given.

Key words: Attachment-detachment reaction; Charge exchange reaction; Collisional ionization reaction; Evaluated rate constants; Flow field kinetics; O_2-N_2 systems.

1. Introduction

In flow field calculations, a number of reactions play a significant role. During the past several years, a concerted effort has been made to obtain the chemical kinetic data needed for such calculations. This study has been an effort to review all such data in detail and thus provide a set of data which would be the best available for calculations. A review carried out a short time ago (Ref. 1)[2] endeavored only to present an opinion which was a concensus among workers that have been using such data over the last few years. Little study was given to the rate constants although, of course, much thought had been given by the individuals originally selecting the values. The present study is an effort to select a set of rate constants based upon a thorough consideration of all available information.

The objective was to obtain the best rate-constant expression for each single reaction with emphasis on data obtained in studies of that isolated reaction. In applied calculations, it may be better to employ those obtained for a complex system of similar application since, to use the rate constants obtained individually, the chemical system must be complete and

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[1] This work was performed for the National Bureau of Standards on Contract CST-373.

[2] References indicate literature citations at the end of this paper.

have accurate rate constants. Otherwise, the somewhat empirical data may be a better representation of the system. Many reviews on these and similar reactions are available, several of which are also specifically applied to re-entry flow fields.

A rate constant may be defined by k in the expression

$$\frac{-d(A)}{dt} = k(A)\ (B)$$

for the rate of the reaction A + B→... The units used are such that they be used with concentrations in molecules cm^{-3}, time in seconds, and temperatures in degrees Kelvin. The rate constants are given here in the form $k = a\ T^b\ e^{-c/T}$. This form can usually be made to fit available data as well as any simple form. The value of c is related to the activation energy. The activation energy of an exothermic reaction may be negligible. If an exothermic reaction has an appropriate activation energy, the reverse endothermic reaction will have an activation energy equal to that of the exothermic reaction plus the heat of the reaction. Although negative activation energies have been reported, these can, at least, be represented by a preexponential negative temperature dependence (negative value of b). The rate constants of reverse reactions are related to the equilibrium constant, K, by

$$K = \frac{k_{forward}}{k_{reverse}}$$

providing the states of each reactant and each product is the same for the reverse as for the forward reaction. If different states are involved, the above reaction does not hold. For most of the reactions considered here, the relation has been applied since it, somewhat surprisingly, appears that the data available make its use reasonable. With the rate constants in this form, the equilibrium constant must be in this form. However, the equilibrium constant is a function of the heat capacity which is commonly expressed by a polynomial. Thus, the equilibrium constant is only approximated by an expression of the form

$$K = A\ T^B\ e^{-C/T}$$

With available data, however, this form is suitable. In some cases, the value of B is negligible. Equilibrium constants for reactions involving ozone were obtained by fitting data from JANAF tables (Ref. 48). Those for the other neutral reactions were taken from Wray (Ref. 23).

The available data for each reaction are discussed in detail. From consideration of these data, a suggested rate constant has been obtained for each reaction. These are given as an expression of the form

$$k = (a \pm \Delta a)\, T^{(b \pm \Delta b)}\, e^{-(c \pm \Delta c)/T}$$

and in graphical form. Data, with little regard for quality are given in tables, but some selection of data was made for the figures. In the graphs, the data considered are also shown together with the suggested rate constant (solid line from 100 to 10,000 K) and upper and lower limits for it (dotted lines). All graphs show the exothermic reaction since it can be shown more accurately. The amount of data on the different reactions varies considerably. One of the major areas of uncertainty is the temperature dependence of the rate constants. For most reactions there are data available at low temperatures for the reaction in the exothermic direction. For a number of the most important reactions, endothermic-direction data are available at high temperatures. For most the the important reactions there are little or no data at intermediate temperatures (from about 500 to 2500 K). The uncertainties in the rate constants are accordingly greatest at the intermediate temperatures. This is difficult to express when the uncertainty in a rate constant is expressed. In fact, this can probably not be done in a reasonable manner when a mathematical expression is given. It can, however, be shown graphically. Thus, while limits are given for each rate constant expression, a more exact and detailed estimate of the uncertainty as a function of temperature could be best seen by an examination of the graphical expression. However, since there is no way to assess the uncertainty accurately, the graphs show the same uncertainty as given by the expression.

The reactions considered in detail include the major reactions usually used in flow field calculations together with collisional ionization processes, ion charge exchange reactions, and attachment and detachment reactions, all for the nitrogen-oxygen system. Also discussed are a few reactions of other species.

The usual major reactions are:

$$O_2 + M \rightarrow O + O + M \qquad M = O_2, N_2, O, N, NO$$

$$N_2 + M \rightarrow N + N + M \qquad M = O_2, N_2, O, N, NO$$

$$NO + M \rightarrow N + O + M \qquad M = O_2, N_2, O, N, NO$$

$$O + N_2 \rightarrow N + NO$$

$$O + NO \rightarrow N + O_2$$

$$N + O \rightarrow NO^+ + e$$

The neutral formation of ozone:

$$O + O_2 + M \rightarrow O_3 + M \qquad M = O_2, N_2, O, N, NO$$

is also included as is the subsequent reaction

$$O + O_3 \rightarrow O_2 + O_2$$

Under certain conditions, collisional ionization can be important. This is mainly the ionization of N_2 and O_2 by collision with these same molecules or with free electrons, leading to the formation of N_2^+ and O_2^+ .

$$N_2 + M \rightarrow N_2^+ + e + M \qquad M = N_2, O_2, e$$

$$O_2 + M \rightarrow O_2^+ + e + M \qquad M = N_2, O_2, e$$

Once these molecular ions are formed, they may recombine with free electron by dissociative recombination. However, they are much more likely to undergo charge exchange reactions. The term charge exchange is used here to include both charge transfer and charged rearrangement (ion-molecule) reactions. The most important of these appear to be

$$N_2^+ + O_2 \rightarrow N_2 + O_2^+$$

$$N_2^+ + NO \rightarrow N_2 + NO^+$$

$$N_2^+ + O \rightarrow NO^+ + N$$

$$O_2^+ + NO \rightarrow O_2 + NO^+$$

Other reactions of these types could play some role but these four should reasonably represent the system.

In cool portions of the wake, negative ions are important. Hence, attachment and detachment reactions were considered. These included:

$$O_2 + e + M \rightarrow O_2^- + M \qquad M = O_2, N_2$$

Other reactions involving negative ions are discussed later.

Nothing is considered on the role of vibrational and electronic excited states.

Vibrationally excited nitrogen persists long after the kinetic temperature has fallen in some cases. This effect is included in some codes on wake calculations but is missing in many. Likewise, some metastable electronic states, such as $O_2(^1\Delta g)$, may be important.

2. Neutral Reactions

$O_2 + M \rightarrow O + O + M$ $\Delta E = 5.12$ eV

The dissociation of oxygen and the reverse three-body atom recombination are probably the most studied of the reactions of interest to re-entry. The collision partners for which the most work has been done and which are of most interest are O_2, O, N_2, and Ar.

The dissociation process with O_2 as the collision partner has been studied at high temperatures by Mathews (Ref. 2), Byron (Ref. 3), Rink (Ref. 4) Wilson (Ref. 5), Schexnayder (Ref. 6), Chesick (Ref. 7), Generalov (Ref. 8), and Eckerman (Ref. 9). The data obtained are shown in (fig. 1) and are listed in (table 1).

In this and succeeding tables, the names of the authors who have studied the reaction in the direction given are underlined.

A recent review by H. S. Johnston considered the available data somewhat differently with slightly different results. It is believed that the present revision put more stress on the high temperature data as seemed appropriate to the application.

The temperature dependence has been studied in several of the high temperature dissociation investigations. While some of these find or suggest a $T^{-1.5}$ dependence, there is by no means general agreement on this. But most serious is the wide difference between the low temperature recombination rate constant values obtained by extrapolating the dissociation data (and using the equilibrium constant) and the values obtained by studies of the recombination at low temperatures. The dissociation data give values which are an order of magnitude or more higher than obtained in the direct recombination studies. This is opposite of what would be most expected of effects of excited electronic or vibrational states unless the reactant excited states are overpopulated in the dissociation studies. This indicates a more complex mechanism than the simple reverse reaction.

In view of the appreciable disagreement in the values, and somewhat the temperature dependencies, obtained in the various high temperature studies, it would seem reasonable not to require a suggested rate constant to fit any of these temperature dependencies, but rather to have it agree reasonably with the most acceptable of the absolute values. Use of such values and those of the low temperature data will give a usable expression for the entire temperature range. It will not agree with any temperature dependence but will fit the

values given by the best data. Since the experimentally determined temperature dependencies can only be said to be approximate or in some cases only guessed because of the lack of any real indication, it is not deemed necessary to use such dependencies. However, it must be noted that all of these dependencies found showed a steeper dependence than that which is suggested to fit both high and low temperature data.

The suggested values are:

$$k_d(O_2) = 1.37 \times 10^{-5}\, T^{-.83}\, e^{-59400/T} \quad cm^3\ particle^{-1} s^{-1}$$

$$k_r(O_2) = 1.9 \times 10^{-32}\, T^{-.33} \quad cm^6\ particle^{-2} s^{-1}$$

The use of one such expression with the above mentioned shortcomings seems preferable to using two expressions, one when the dissociation predominates and one when the recombination predominates. Either is an empirical solution and the suggested values fit the most acceptable data well, although obviously more work is needed especially at intermediate temperatures. A polynomial form may be needed for some rate constants.

For C_2 as the collision partner, the rate constant is probably accurate to a factor of three at high temperature and at least that accurately, or perhaps a factor of two, at low temperature. However, at intermediate temperatures, the uncertainty is greater, perhaps a factor of five. Thus, the stated uncertainty of the suggested rate constant of a factor of three may be optimistic at the intermediate temperatures.

With atomic oxygen as the collision partner, only high temperature data are available. These data, obtained by Byron (Ref. 3), Camac (Ref. 10), Rink (Ref. 4), and Wilson (Ref. 5), are shown in figure 2. The data were obtained in shock tubes by density measurements or by U-V absorption measurements. Wray has evaluated the various data and has selected a compromise value for this. The compromise is reasonable and agrees well with the absolute values at the high temperatures and compromises the temperature dependencies. These rate constants are:

$$k_d(O) = 1.5 \times 10^{-4}\, T^{-1}\, e^{-59400/T}$$

$$k_d(O) = 2.1 \times 10^{-31}\, T^{-1/2}$$

Data for the case of argon as the collision partner have been obtained by Byron (Ref. 3), Camac (Ref. 10), Rink (Ref. 4), Wray (Ref. 11), Schexnayder (Ref. 6), and Generalov (Ref. 8), all dissociation studies at high temperature studies, and recombination studies by Wray at intermediate temperatures and by Campbell and Thrush (Ref. 12) and by Marshall (Ref. 13) at

low temperatures. These data are shown in figure 3. The temperature dependencies found by the various studies disagree as do some of the absolute values.

A reasonable average curve can be drawn through these data which is in reasonable agreement with most of these. The expression $3.3 \times 10^{-30} T^{-1.3}$ fits in this way. It is a reasonable compromise of the data with most weight being given to the data of Wray (Ref. 11). Since this reaction is of little importance itself and the application of the data to other collision partners is questionable, the expressions fitting the data as shown is suggested:

$$k_d(Ar) = 2.4 \times 10^{-3}\ T^{-1.8}\ e^{-59400/T}$$

$$k_r(Ar) = 3.3 \times 10^{-30}\ T^{-1.3}$$

With nitrogen as a collision partner, most of the available data (fig. 4) are low temperature recombination data. These are from the work of Campbell and Thrush (Ref. 12) whose data over the range of 196 to 327°K predict approximately a T^{-2} dependence. Morgan's data (Ref. 14) at 300°K agrees well with these data. The only high temperature data are those of Generalov (Ref. 8). For want of any more suitable data, they are used to obtain a temperature dependence. The suggested values are:

$$k_d(N_2) = 2.2 \times 10^{-3}\ T^{-1.7}\ e^{-59400/T}$$

$$k_r(N_2) = 3 \times 10^{-30}\ T^{-1.2}$$

It is obvious that more data are needed. This case (N_2) appears to have a rate constant as high as that for O_2 as the collision partner, at least at low temperatures. It is probably of more importance and many less data are available for it.

For these dissociation rate expressions, the preexponential term is, at low temperatures, higher than the collision frequency ($\sim 10^{-10}$). This can not be explained. Their use is justified only by the data fit.

Table 1. $O + O + M \rightarrow O_2 + M$

M	Author	Ref.	k_r (cm^6 particle^{-2} sec.$^{-1}$)	T(K)
O_2	Barth	15	8.2×10^{-33}	300
	Byron	3	$4.54 \times 10^{-30}\ T^{-1}$	2800 - 5000
	Camac	10	$\leq 2.5 \times 10^{-32}\ T^{-1/2}$	6000 - 7000
	Chesick	7	3.3×10^{-33}	3100
	Chesick	7	1.3×10^{-33}	3500
	Eckerman	9	$3.72 \times 10^{-30} T^{-1}$	4000 - 7000

Table 1. $O + O + M \rightarrow O_2 + M$—continued.

M	Author	Ref.	k_r ($cm.^6$ particle^{-2} sec.$^{-1}$)	T(K)
	Elias	16	$<1.1 \times 10^{-33}$	293
	Generalov	8	$1.33 \times 10^{-22} T^{-3}$	2600 - 7000
	Golden	17	3.3×10^{-33}	300
	Hall (Byron data)	18	$8.3 \times 10^{-34} T^{-1}$	2800 - 5000
	Kiefer	19	$2.3 \times 10^{-29} T^{-1.22}$	1500 - 2800
	Kretschmer	20	5.55×10^{-34}	350
	Krongelb	21	1.39×10^{-32}	300
	Losev	22	5.55×10^{-34}	300
	Marshall	13	2.2×10^{-33}	300
	Mathews	2	$2.53 \times 10^{-26} T^{-2}$	3000 - 5000
	Rink	4	$4.44 \times 10^{-30} T^{-1}$	3000 - 6000
	Schexnayder	6	$2.08 \times 10^{-37} T^{.5} e^{22000/T}$	5000 - 10000
	Wilson	5	$6.94 \times 10^{-30} T^{-1}$	2700
	Wray	23	$7.5 \times 10^{-32} T^{-1/2}$	Review
	Langan	24	$2.44 \times 10^{-33} T^{-.44}$	Review
O	Byron	3	2.71×10^{-33}	2800 - 5000
	Camac	10	$1.47 \times 10^{-27} T^{-1.5}$	5000 - 7000
	Hall (Byron data)	18	4.9×10^{-33}	2800 - 5000
	Rink	4	$1.33 \times 10^{-29} T^{-1}$	3000 - 6000
	Wilson	5	$2.08 \times 10^{-29} T^{-1}$	2700
	Wray	23	$2.08 \times 10^{-31} T^{-1/2}$	Review
N_2	Campbell	12	$4.44 \times 10^{-26} T^{-2.9}$	196 - 327
	Campbell	12	$2.78 \times 10^{-34} e^{713/T}$	196 - 327
	Generalov	8	$8.33 \times 10^{-33} T^{-1}$	3700 - 7000
	Kaufman	25	$4.60 \times 10^{-26} T^{-2.9}$	Review
	Baurer	26	$6.08 \times 10^{-28} T^{-2.5}$	Review

Table 1. $0 + 0 + M \rightarrow O_2 + M$—continued.

M	Author	Ref.	k_r (cm.^{6} particle^{-2} sec.$^{-1}$)	T(K)
N_2	Morgan	14	3.23×10^{-33}	300
	Wray	23	$1.67 \times 10^{-32} T^{-.5}$	Review
Ar	Anderson (by Wray)	27	$1.4 \times 10^{-33} T^{-.5}$	300 - 3000
	Byron	3	1.18×10^{-34}	2800 - 5000
	Camac	10	$8.35 \times 10^{-33} T^{-.5}$	3300 - 7500
	Campbell	12	6.05×10^{-33}	196
	Campbell	12	1.67×10^{-33}	300
	Generalov	8	$1.56 \times 10^{-23} T^{-3}$	2600 - 7000
	Marshall	13	1.8×10^{-33}	300
	Rink	4	$1.30 \times 10^{-30} T^{-1}$	3000 - 6000
	Schexnayder	6	$4.44 \times 10^{-38} T^{.5} e^{21800/T}$	5000 - 10000
	Schexnayder	6	$5.09 \times 10^{-37} T^{.5} e^{7600/T}$	5000 - 7500
	Wray	11	5.8×10^{-35}	1340 - 2920
	Wray	23	$6.7 \times 10^{-37} T^{.5}$	5000 - 11000
	Wray	28	$2.5 \times 10^{-30} T^{-1.5}$	5000 - 11000
	Wray	29	5.83×10^{-35}	5000 - 11000

Table 1. $O_2 + M \rightarrow 0 + 0 + M$

M	Author	Ref.	k_d (cm.^{3} particle^{-1} sec.$^{-1}$)	T(K)
O_2	Byron	3	$3.27 \times 10^{-3} T^{-1.5} e^{-59400/T}$	2800 - 5000
	Camac	10	$1.80 \times 10^{-5} T^{-1} e^{-59400/T}$	6000 - 7000
	Chesick	7	2.3×10^{-16}	3100
	Chesick	7	6.8×10^{-16}	3500
	Eckerman	7	$2.68 \times 10^{-3} T^{-1.5} e^{-59400/T}$	4000 - 7000
	Generalov	8	$9.55 \times 10^{4} T^{-3.5} e^{-59400/T}$	2600 - 7000
	Hall (Byron data)	18	$6.3 \times 10^{-3} T^{-1.5} e^{-59400/T}$	2800 - 5000
	Langan	24	$4.17 \times 10^{-8} T^{-.5} e^{-59400/T}$	Review
	Mathews	2	$1.82 \times 10^{1} T^{-2.5} e^{-59400/T}$	3000 - 5000

Table 1. $O_2 + M \rightarrow O + O + M$—continued.

M	Author	Ref.	k_d ($cm.^3$ $particle^{-1}$ $sec.^{-1}$)	T(K)
O_2	Rink	4	$3.2 \times 10^{-3} T^{-1.5} e^{-59400/T}$	3000 - 6000
	Schexnayder	6	$1.5 \times 10^{-10} e^{-37400/T}$	5000 - 10000
	Wilson	5	$5.0 \times 10^{-3} T^{-1.5} e^{-59400/T}$	2700
	Wray	23	$5.4 \times 16^{-5} T^{-1} e^{-59400/T}$	Review
O	Byron	3	$1.95 \times 10^{-6} T^{-0.5} e^{-59400/T}$	2800 - 5000
	Camac	10	$1.06 \times 10^{0} T^{-2} e^{-59400/T}$	5000 - 7000
	Hall (Byron Data)	18	$3.5 \times 10^{-6} T^{-.5} e^{-59400/T}$	3000 - 5000
	Rink	4	$9.6 \times 10^{-3} T^{-1.5} e^{-59400/T}$	3000 - 6000
	Wilson	5	$1.5 \times 10^{-2} T^{-1.5} e^{-59400/T}$	2700
	Wray	23	$1.5 \times 10^{-4} T^{-1} e^{-59400/T}$	5000 - 7000
N_2	Generalov	8	$1.68 \times 10^{4} T^{-35} e^{-59400/T}$	2000 - 7000
	Baurer	26	$4.37 \times 10^{-1} T^{-3} e^{-59400/T}$	Review
	Wray	23	$1.2 \times 10^{-5} T^{-1} e^{-59400/T}$	Review
Ar	Anderson (by Wray)	27	$3.0 \times 10^{-6} T^{-1} e^{-59400/T}$	350 - 3000
	Byron	3	$8.52 \times 10^{-8} T^{-.5} e^{-59400/T}$	2800 - 5000
	Camac	10	$6.01 \times 10^{-6} T^{-1} e^{-59400/T}$	3300 - 7500
	Generalov	8	$1.12 \times 10^{4} T^{-3.5} e^{-59400/T}$	2000 - 7000
	Rink	4	$9.4 \times 10^{-4} T^{-1.5} e^{-59400/T}$	3000 - 6000
	Schexnayder	6	$3.2 \times 10^{-11} e^{-37600/T}$	5000 - 10000
	Schexnayder	6	$3.06 \times 10^{-10} e^{-51800/T}$	5000 - 7500
	Wray	23	$4.2 \times 10^{-8} T^{-.5} e^{-59400/T}$	1340 - 2920
	Wray	23	$4.83 \times 10^{-10} e^{-59400/T}$	5000 - 11000

$N_2 + N_2 \rightleftharpoons N + N + N_2$ $\Delta E = 9.76$ eV

This reaction has been studied in both the dissociation and recombination directions. The considerable disagreement among the various results is evident in figure 5. The results on the dissociation reaction are from the work of Cary (Ref. 30) and of Byron (Ref. 31), each of which used a shock tube following the reaction by interferometric measurements. In the original statements of results, there was only approximately a factor of up to 1.4 disagreement in the rate coefficients in the temperature range covered but a major disagreement in the temperature dependence. Byron reinterpreted Cary's data and improved this situation slightly. Byron's analyses of his and Cary's data are marked Byron/Cary in the figures. Although the source of this disagreement in the absolute values is difficult to determine, it is not serious enough to be of great concern. However, that of the temperature dependence is serious. In order to further investigate this, the recombination data must be considered.

The low temperature values stretch over an order of magnitude of 300 K (from 2.2×10^{-33} to 1.7×10^{-32} cm^6 $particle^{-2}$ sec^{-1}). Two studies have reported temperature dependences, one of T^{-2}, the other of T^0. Most of the low temperature data have been obtained from flow discharge systems. In a recent study, Evensen and Burch (Ref. 32) used both a flowing and a static system. The more reliable results were obtained in the static system from which they obtained a value of 1.12×10^{-32} at 300 K. They used an electron spin resonance technique and found no evidence for the formation of excited atoms in the afterglow during the measurements although ground state atoms may be formed then. Campbell and Thrush (Ref. 33) in another recent study using titration techniques studied the reaction from 196 to 327 K and found a rather steep decrease in rate with increasing temperature. With these data, they expressed the rate constant by 3.33×10^{-27} and by 8.33×10^{-34} $e^{490/T}$. These both fit their data well but give drastically different values at high temperatures. The expression with the negative activation energy fits both their data and the high temperature data within a factor of two but shows practically no temperature dependence at the high temperatures. It would in all likelihood be a poor expression to use at intermediate temperatures. Herron (Ref. 34) found no effect of temperature on this rate constant over a range of 273 - 453 K. He did, however obtain a value of 1.7×10^{-32} at 197 K. Although he believes this to be in error, it may indicate

a temperature dependence similar to Campbell's at low temperatures. Other low temperature data lie above the Campbell and Thrush data by a factor of 2 to 4. These data, all at 300 K, give recombination rate constants, shown in Table II along with the expressions obtained using the dissociation rate constant and the equilibrium constant. Data for He and Ne as collision partners are also available in the work of Cary (Ref. 30), of Campbell and Thrush (Ref. 33), and of Herron et al (Ref. 34). The other interesting collision partner is the free electron which Bradt (Ref. 35) reports to be 10^7 to 10^8 times as effective as N_2 in the recombination. If so, this may be of some importance to re-entry.

It is difficult to reconcile the high temperature and the low temperature data and their temperature dependences. It appears that the processes change as the temperature changes and that quite possibly in the obtention of certain of the data, the distribution of excited states did not follow the Boltzmann distribution appropriate to the kinetic temperature. Since there are drastically differing data in each range, it would appear reasonable to select a temperature dependence which goes through the data at each end rather than agreeing with one of the stated temperature dependences. A rate constant of $7.7 \times 10^{-31} T^{-.75}$ has been chosen. This fits all data within a factor of two (although it is not thought that such is necessary since not all data available are thought to be that accurate) except the data of Campbell and Thrush (Ref. 33) which are within a factor of three. It seems likely that these data show the large temperature dependence because of certain effects which make it different from the reverse of the high temperature dissociation. It seemed preferable to use the data of Evensen and Burch (Ref. 32) and at the same time to come closer to such data as that of Marshall (Ref. 13), of Herron et al (Ref. 34)(as well as closer to others). A factor of three appears reasonable for the uncertainty although it may be larger in the 500 - 3000 K range.

This recombination rate constant when used with the equilibrium constant gives a dissociation rate constant of

$$k_d(N_2) = 8.3 \times 10^{-6 \pm .5} T^{-.75} e^{-113200/T}$$

This, of course, agrees with the high temperature dissociation data in the same way that the recombination rate constant agrees with the high temperature recombination data obtained from the dissociation data.

$N_2 + N \rightarrow N + N + N$ $\Delta E = 9.76$ eV

There are many fewer data for the dissociation or recombination with atomic nitrogen as a collision partner than for the case of molecular nitrogen. Once again, Byron (Ref. 31) and Cary (Ref. 30) obtained data. The only other data are that of Allen (Ref. 36) at 6400. These data are shown in Table II and Figure 6 along with the compromise suggested by Byron (Ref. 31). The last is a result of Byron's reinterpreting Cary's data considering it as well as his own. Wray and Byron (Ref. 37) suggested that Cary's data might be looked at in more detail but no such action has been reported. Until this is done and the two investigations once again considered jointly, it is suggested that Byron's compromise be used for this rate constant. For dissociation and recombination, this would be

$$k_d(N) = 5 \times 10^{-2 \pm .6} T^{-1.5} e^{-113200/T}$$

$$k_r(N) = 4.6 \times 10^{-27 \pm .6} T^{-1.5}$$

$N_2 + Ar \rightarrow N + N + Ar$ $\Delta E = 9.76$ eV

This reaction with argon as the collision partner is not important in itself. However, the rate constants are usually applied to the cases of all collision partners except N_2 and N - i.e., for O_2, O, NO, etc. There is no direct justification for this other than that such has been done and to the limited extent that it can be determined, it seems to fit calculations when a particular set of rate constants are used. There is, of course, no basis for supporting this to be correct and that a fit would be obtained when different rate constants are used for other reactions. Nevertheless, it appears that calculations would not have been successful if the rate constants for the cases of O, O_2, and NO are much higher than that of argon. If they are lower they would have little effect. Thus, the use of the argon rate constant seems reasonable although somewhat on the empirical side.

There are both dissociation and recombination data with argon as the collision partner, the former being obtained by Byron (Ref. 31) and by Cary (Ref. 30), the latter by Herron, Franklin, Bradt and Dibeler (Ref. 34) (at 300 K), by Campbell and Thrush (Ref. 33) (196-327 K) and by Harteck, Reeves and Mannella (Ref. 38) (at 300 K). These data are shown in fig. 7

all in terms of the recombination rate constant. Once again there are disagreements in both absolute values and temperature dependences in both the high and low temperature data. The suggested value is a compromise of the high temperature data in that range and agrees with Herron's and with Campbell's data at 300 K. It does not agree with Campbell's temperature dependence or with Harteck's results. The suggested rate constants are

$$k_d(Ar) = 4.8 \times 10^{-6 \pm 0.5}\, T^{-.82}\, e^{-113200/T}$$

$$k_r(Ar) = 4.4 \times 10^{-31 \pm 0.5}\, T^{-.82}$$

Table II. $N + N + M \rightarrow N_2 + M$

$M = N_2$	Ref.	k_r (cm^6 particle^{-2} sec^{-1})	T (K)
Allen	36	$< 1.4 \times 10^{-33}$	6400
Barth	15	7.0×10^{-33}	300
Campbell	33	$3.33 \times 10^{-27}\, T^{-2}$	197 - 327
Evenson	32	1.12×10^{-32}	300
Harteck	38	1.72×10^{-32}	300
Herron	34	7.9×10^{-33}	273 - 453
Kretschmer	39	2.2×10^{-33}	350
Marshall	13	7.5×10^{-33}	300
Mavroyannis	40	1.4×10^{-32}	300
Wentink	41	1.7×10^{-32}	300
Byron	31	$7.73 \times 10^{-32}\, T^{-.5}$	6000 - 9000
Cary	30	$3.45 \times 10^{-27}\, T^{-1.7}$	6000 - 10000
Byron & Cary(Byron)	31	$7.4 \times 10^{-28}\, T^{-1.5}$	6000 - 10000

M = N	Ref.	k_r (cm^6 particle^{-2} s^{-1})	T (K)
Allen	36	1.8×10^{-32}	6400
Byron	31	$6.6 \times 10^{-27}\, T^{-1.5}$	6000 - 9000
Cary	30	$2.5 \times 10^{-29}\, T^{-1}$	6000 - 10000
Byron & Cary(Byron)	31	$4.6 \times 10^{-27}\, T^{-1.5}$	6000 - 10000

M = Ar	Ref.	k_r (cm^6 particle^{-2} s^{-1})	T (K)
Byron	31	$2.84 \times 10^{-32} T^{-.5}$	6000 - 9000
Cary	30	$1.6 \times 10^{-30} T^{-1}$	6000 - 10000
Byron & Cary(Byron)	31	$9.3 \times 10^{-33} T^{-.5}$	6000 - 10000
Campbell	33	$3.33 \times 10^{-27} T^{-2}$	197 - 327
Harteck	38	1.72×10^{-32}	300
Herron	34	3.9×10^{-33}	273 - 453

$N_2 + M \rightarrow N + N + M$

M = N_2	Ref.	k_d (cm^3 particle^{-1} s^{-1})	T (K)
Byron	31	$8.0 \times 10^{-7} T^{-.5} e^{-113200/T}$	6000 - 9000
Cary	30	$3.73 \times 10^{-2} T^{-1.7} e^{-113200/T}$	6000 - 10000
Byron & Cary(Byron)	31	$8.0 \times 10^{-3} T^{-1.5} e^{-113200/T}$	6000 - 10000
Appleton	119	$6.2 \times 10^{-3} T^{-1.6} e^{-113200/T}$	8000 - 15000
M = N			
Byron	31	$7.17 \times 10^{-2} T^{-1.5} e^{-113200/T}$	6000 - 9000
Cary	30	$2.71 \times 10^{-4} T^{-1} e^{-113200/T}$	6000 - 10000
Byron & Cary(Byron)	31	$5.0 \times 10^{-2} T^{-1.5} e^{-113200/T}$	6000 - 10000
Appleton	119	$2.7 \times 10^{-2} T^{-1.6} e^{-113200/T}$	8000 - 15000
M = Ar			
Byron	31	$3.17 \times 10^{-7} T^{-.5} e^{-113200/T}$	6000 - 9000
Cary	30	$1.73 \times 10^{-5} T^{-1} e^{-113200/T}$	6000 - 10000
Byron & Cary(Byron)	31	$1.0 \times 10^{-7} T^{-.5} e^{-113200/T}$	6000 - 10000
Appleton	119	$2.3 \times 10^{-3} T^{-1.6} e^{-113200/T}$	8000 - 15000

$NO + M \rightarrow N + O + M$ $\Delta E = 6.51$ eV

Data for the dissociation of NO with NO as the collision partner have been obtained by Freedman (Ref. 42), by Wray (Ref. 43), and by Allport (Ref. 44). Freedman and Allport each obtained a temperature dependence which he expressed as an activation energy which was considerably less than the reaction energy, and which when combined with the equilibrium constant gave a large negative activation energy for the recombination reaction. These data shown in figure 8 are probably for a more complex chemical system than given by the straight dissociation reaction. Expressing the temperature dependence as a negative preexponential temperature dependence would also not appear realistic. Wray's results are used as the suggested rate constants.

The three-body formation of NO with nitrogen as a catalyst has been studied as low temperatures by Campbell and Thrush (Ref. 12),by Mavroyannis and Winkler (Ref. 40) and by Kretschmer and Petersen (Ref. 39). Campbell obtained data from 197 to 327 K. He interprets his data in terms of two different temperature dependences. No high temperature data are available. Wray (Ref. 43) has assumed that his data obtained for the case of argon as the collision partner hold for N_2 as the collision partner and has found a fit in calculations using it this way. These data indicate a $T^{-1.5}$ temperature dependence which, if extrapolated, would be orders of magnitude higher than the Campbell data at low temperatures. Since the high temperature data were not obtained with N_2, it is suggested that the temperature dependence be ignored and a constant value of 1.1×10^{-32} be used although it is not likely that there is no temperature dependence. The available data are shown in fig. 9.

For other third bodies of interest, mainly O_2 and O, it is suggested that these same rate constants be used. It is very difficult to correlate the dissociation and recombination data for argon as the collision partner (fig. 10). The data of Campbell and Thrush (Ref. 12) at low temperatures and of Wray and Teare (Ref. 43) at high temperatures are shown in fig. 10.

Recommended values for the rate constants are:

M	k_d	k_r
NO	$1.32 \times 10^{-2\pm.6} T^{-1.5} e^{-75400/T}$	$9.1 \times 10^{-26\pm.6} T^{-1.5}$
N_2	$1.5 \times 10^{-9\pm.5} e^{-75400/T}$	$1.1 \times 10^{-32\pm.5}$
Ar	$3.5 \times 10^{-8\pm.5} T^{-.6} e^{-75400/T}$	$2.4 \times 10^{-31\pm.5} T^{-.6}$

$O + O_2 + M \rightarrow O_3 + M$ $\Delta E = -1.05$ eV

This reaction has been investigated in detail for various collision partners. Both the recombination and the dissociation reaction have been studied, often together with the reaction $O + O_3 \rightarrow O_2 + O_2$ Data are shown in Figures 11-13 and Table III. Some of the data have been obtained at ratios of rate constants and some involve use of the equilibrium constant. There is uncertainty enough in the heat of formation of ozone to cause a factor of two uncertainty in the rate constants acquired by use of the equilibrium constants.

Glissman and Schumacher (Ref. 45) obtained ozone dissociation data over thirty years ago over a temperature range of 343 - 383 K which may still be regarded as reliable. Their data were O_3, O_2, N_2, Ar, CO_2 and He as collision partners. More recently Benson and Axworthy (Ref. 46) analyzed these data and added their own data at one temperature, 373 K. They also treated several collision partners, obtaining data in good agreement with the earlier work. High temperature (689 - 910 K) data were obtained in a shock tube by Jones and Davidson (Ref. 47) using N_2 and Ar as collision partners. These dissociation data have been used (for the temperature ranges over which the data were obtained) in this study together with equilibrium constant data from the JANAF Tables (Ref. 48) to obtain recombination rate constants. Their agreement with the recombination reaction data as such indicates that there are no large effects of metastable states in these data.

Zaslowsky and coworkers (Ref. 49) obtained dissociation rate data with O_3 as a collision partner and also obtained data which they interpreted in terms of recombination with O_2 as a collision partner. (Ref. 50) From the latter data, a rate constant of $4.0 \times 10^{-34} e^{-150/T}$ was obtained for the temperature range of 213 - 243 K.

Data have been obtained on the recombination reactions using oxygen atoms generated in several ways. One of the most serious problems is the possibility of creating excited atoms and molecules when creating atoms. Another problem is the presence of impurities which react rapidly with the oxygen atoms.

A very careful experiment was carried out by Kaufman and Kelso (Ref. 51, 52) at 300 K with N_2 and O_2 as collision partners. They obtained values of 5.5 and 6.5×10^{-34} cm^6 $molecule^{-2}$ s^{-1} respectively. Although some of their experiments were carried out using oxygen from a discharge, they regard their results obtained using atomic oxygen from the thermal decomposition of ozone as much more reliable and the quoted result is from those data. The problem of excited O_2 and N_2 is considered by Schiff and coworkers (Ref. 16, 53-55)

who obtained a rate constant for the dissociation of ozone by excited nitrogen.

Clyne, McKenney, and Thrush (Ref. 56) obtained recombination data over the temperature range 188 - 373 K for Ar as the collision partner. Their data can be fitted over this range by the expression $1.48 \times 10^{-25} T^{-3.4}$ cm^6 particle^{-2} s^{-1} Sauer and Dorfman (Ref. 57) obtained a rate constant of 2.36×10^{-34} at 296 K with Ar forming the atomic oxygen by pulses of high energy electrons. They present arguments for the lack of effects of electronically excited species but the arguments are not conclusive.

In re-entry, the formation of ozone is of more interest than its dissociation. The most reliable data appears to be that of Kaufman for N_2 and O_2 as collision partners. For other collision partners, the data of Benson and Axworthy and Glissman and Schumacher may be used. The high temperature data of Jones and Davidson are usable to obtain a temperature dependence. Figure 11 shows the various data for $O + O_2 + N_2 \rightarrow O_3 + N_2$ together with a recommended rate constant of $k_r (N_2) = 4.5 \times 10^{-29} \pm .6\ T^{-2}$ and figure 13 shows the data for Ar as the collision partner with the recommended $k_r(Ar) = 2.9 \times 10^{-29} \pm .6\ T^{-2}$. Data are listed in Table III.

Table III. $O + O_2 + M \rightarrow O_3 + M$

M	Author	Ref	k_r(cm^6 particle^{-2} s^{-1})	T(K)
N_2	Benson & Axworthy	46	2.53×10^{-34}	373
N_2	Glissman & Schumacher	45	$3.9 \times 10^{-31} T^{-1.24}$	343 - 383
N_2	Kaufman	51,52	5.5×10^{-34}	300
N_2	Jones & Davidson	47	$1.15 \times 10^{-29} T^{-1.80}$	689 - 963
Ar	Glissman & Schumacher	45	$2.46 \times 10^{-31} T^{-1.24}$	343 - 383
Ar	Clyne, McKenney & Thrush	56	$1.48 \times 10^{-25} T^{-3.4}$	188 - 373
Ar	Sauer & Dorfman	57	2.28×10^{-34}	296
Ar	Jones & Davidson	47	$2.15 \times 10^{-27} T^{-2.64}$	769 - 910
O_2	Kaufman	51,52	6.5×10^{-34}	300
O_2	Benson & Axworthy	46	2.71×10^{-34}	373
O_2	Glissman & Schumacher	45	$4.3 \times 10^{-31} T^{-1.24}$	343 - 373
O_2	Hacker	58	7.0×10^{-34}	300

Table III. $O + O_2 + M \rightarrow O_3 + M$—continued

M	Author	Ref.	k_r(cm^6 particle^{-2} s^{-1})	T(K)
O_2	Dickens	59	3.0×10^{-34}	283
O_2	Krongelb & Strandberg	21	3.0×10^{-34}	350
O_2	Urbach & Zaslowsky	49,50	$4.0 \times 10^{-34}\ e^{-150/T}$	213 - 243

$N + NO \rightarrow N_2 + O$ $\Delta E = -3.25$ eV

This reaction has been studied at about 300 K by Phillips and Schiff (Ref. 60), by Herron (Ref. 61,62), by Verbeke and Winckler (Ref. 63), by Harteck and Dondes (Ref. 64), by Kaufman and Kelso (Ref. 65, 66) and by Kistiakowsky and Volpi (Ref. 67, 68) at somewhat elevated temperature by Clyne and Thrush (Ref. 69, 70) and in the reverse direction at high temperatures by Glick, Klein and Squire (Ref. 71). The results of these studies are listed in Table IV and are shown in figure 14. The early studies by Kaufman and by Kistiakowsky obtained lower limits. Phillips and Schiff used a mass spectrometer for species determination in a flow system. They obtained a rate constant of $(2.2 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}. The data of Clyne and Thrush over the temperature range of 476 - 755 K were fit by $(5.0 \pm 1.0) \times 10^{-11}\ e^{(-100 \pm 350)/T}$. The data were obtained indirectly from a ratio of the rate constant of this reaction to that of the $N + O_2$ reaction. The data of Glick were obtained for the reverse ($O + N_2$) reaction in shock tube studies. Their data have been re-examined by Duff who suggests a rate constant of $8.2 \times 10^{-11}\ e^{-38000/T}$ to fit them. The available data show that there is no significant temperature dependence for the rate constant of the N + NO reaction. The rate constant suggested for use is that of Phillips and Schiff which may be assumed to hold at all temperatures. This fits the data of Clyne and Thrush and those of Glick, Klein and Squire with the equilibrium constant well. Thus the recommended rate constants for the reverse and forward reactions are:

$$O + N_2 \rightarrow N + NO \quad k = 1 \times 10^{-10 \pm .3}\ e^{-38000/T}\ cm^3 mol^{-1} sec^{-1}$$

and

$$N + NO \rightarrow O + N_2 \quad k = 2.2 \times 10^{-11 \pm .3}$$

Table IV. $N + NO \rightarrow N_2 + O$

Author	Ref	k (cm^3 particle^{-1} sec^{-1})	T(K)
Clyne	69,70	$5 \times 10^{-11} e^{-100/T}$	476 - 755
Kaufman	25	2.22×10^{-11}	Review
Harteck	64	3×10^{-13}	300
Herron	61,62	1.7×10^{-11}	300
Kaufman	65,66,74	6.7×10^{-12}	1572 - 1690
Kistiakowsky	67,68	7.67×10^{-12}	394 - 517
Phillips	60	2.2×10^{-11}	298
Verbeke	63	4.3×10^{-12}	300
$O + N_2 \rightarrow NO + N$			
Glick, Klein, Squire	71	$1.8 \times 10^{-12} T^{.5} e^{-37000/T}$	2000 - 3000
Wray (Glick data)	23	$8.2 \times 10^{-11} e^{-38000/T}$	
$N + O_2 \rightarrow O + NO$		$\Delta E = 1.39$ eV	

This reaction has been investigated most often together with the $N + NO \rightarrow O + N_2$ reaction. The exothermic reaction has been studied at temperatures ranging from 300 to 755 K while the reverse reaction has been studied at higher temperatures. The data are shown in Table V.

The data of Clyne and Thrush (Ref. 69,70), of Kistiakowsky and Volpi (Ref. 67) and of Mavroyannis and Winkler (Ref. 72) agree well and cover the temperature range of 394 - 755 K. The more recent data of Wilson (Ref. 72a) also agree. These cover a wider range (300 - 910 K). These can be seen in figure 15. The data of Harteck & Dondes (Ref. 64) and of Kretschmer and Petersen (Ref. 39) are uncertain. At high temperatures, the data of Wray & Teare (Ref. 43) obtained from 3000 to 8000 K by analysis of a complex system in an NO shock tube study is more accurate at about 5000 K. The data of Sulzmann & Ludwig (Ref. 73) require the use of several other rate constants that were not well established at the time of their work. The data of Kaufman & Decker (Ref. 74) provide reliable intermediate

temperature data. It appears that the data for the rate constant for this reaction are dependable and a fit of these data is accurate to a factor of two over the temperature range Kaufman has obtained a slightly better fit (Ref. 25) to the low temperature data than given by the suggested expression but the latter is used since there is also much importance to this pair of reactions at high temperatures. The suggested value for the exothermic reaction is:

$$k = 3 \times 10^{-16} \pm .3\ T^{1.5}\ e^{-3000/T}$$

and for the reverse reaction, $O + NO \rightarrow N + O_2$

$$k = 7.2 \times 10^{-17} \pm .3\ T^{1.5}\ e^{-19100/T}$$

$N + O_2 \rightarrow O + NO$

Author	Ref.	k (cm^3 particle^{-1} sec^{-1})	T(K)
Clyne & Thrush	69,70	$1.4 \times 10^{-11}\ e^{-3570/T}$	412 - 755
Harteck & Dondes	64	1×10^{-16}	300
Kistiakowsky & Volpi	67	$3.3 \times 10^{-12}\ e^{-3120/T}$	394 - 517
Kretschmer & Petersen	39	8.3×10^{-17}	350
Wilson	72a	$1.41 \times 10^{17}\ e^{-3980/T}$	300 - 910

$O + NO \rightarrow N + O_2$

Kaufman & Decker	74	$6 \times 10^{-12}\ e^{-19900/T}$	1572 - 1690
Kaufman & Kelso	65	$1.4 \times 10^{-11}\ e^{-20400/T}$	1170 - 1530
Wray & Teare	43	$5.3 \times 10^{-15}\ T\ e^{-19680/T}$	5000
Sulzmann & Ludwig	73	$3.4^{-14}\ T^{1/2}\ e^{-19200/T}$	2250 - 3450

$O + O_3 \rightarrow O_2 + O_2$ $\quad \Delta E = -4.06$ eV

This reaction has been studied in conjunction with ozone dissociation and its three-body formation, $O_3 + M \rightarrow O + O_2 + M$. In most cases the data obtained have been for a ratio of the $O + O_3$ rate constant to that of one of the others or to the equilibrium constant for the above reaction. Since the heat of formation of ozone is in doubt by about 0.4 kcal/mole (Ref. 48), the rate constant of the $O + O_3$ is uncertain by about a factor of two because of

this. Data were obtained for this reaction together with data for the dissociation by Benson and Axworthy (Ref. 46), by Glissman and Schumacher (Ref. 45) with further evaluation by Castellano and Schumacher (Ref. 75), by Zaslowsky and co-workers (Ref. 49,50), by Pshezhetskii and co-workers (Ref. 76), and, at higher temperatures, by Jones and Davidson (Ref. 47). Data were obtained in a recombining system by Clyne and co-workers (Ref. 56). In a flow discharge system, Phillips and Schiff (Ref. 60) obtained direct data on the $O + O_3$ reaction. Harteck and Dondes (Ref. 77) obtained a match for data in a complex system using assumed rate constants. The data are shown in figure 16 and listed in table VI. Some of the comments made about certain investigations on the $O_3 + M \rightleftarrows O + O_2 + M$ reaction apply here.

The most reliable data are probably those of Schumacher with their various interpretations (Benson, Castellano). These are taken together with those high temperature data of Jones and Davidson to get the suggested rate constant. It is interesting that the extrapolation of the Schumacher data, using their temperature dependence, gives excellent agreement with Jones' data. Other data do not agree too well with this and it is rather perplexing that Phillips data fall this far out of line although there is a possible effect of water vapor.

These considerations lead to a recommended value for the rate constant of the exothermic reaction, $O + O_3 \rightarrow O_2 + O_2$.

$$k = 3.6 \times 10^{-11} \pm .7 \; e^{-2750/T}$$

which leads to a rate constant of

$$k = 2.7 \times 10^{-9} \pm .7 \; T^{-.5} \; e^{-50190/T}$$

for the reverse reaction. Considering the uncertainties in the experimental data and that in the equilibrium constant, the uncertainty is estimated as a factor of five although it may be somewhat lower at low temperatures.

It is quite possible that much of the ozone data involves excited O or O_2 and, thus, is not applicable for much of the manipulations among the various rate constants which are required to obtain the rate constants of individual reactions. The data were used here, however, since excited states are in all likelihood present in the reentry system although admittedly in much different amounts.

Table VI. Data on $O + O_3 \rightarrow O_2 + O_2$

Author	Ref.	$k(cm^3\ particle^{-1}\ s^{-1})$	T(K)
Benson & Axworthy	46	$5.6 \times 10^{-11}\ e^{-2870/T}$	373
Campbell & Nudelman	78	$9.0 \times 10^{-12}\ e^{-2133/T}$	Review
Castellano & Schumacher	75	$5.62 \times 10^{-11}\ e^{-2870/T}$	278 - 298
Clyne, McKenney & Thrush	56	$1.0 \times 10^{-11}\ e^{-4300/T}$	180 - 1000
Clyne, Thrush & Wayne	79	$8 \pm 1 \times 10^{-14}$	300
Harteck & Dondes	77	$2.0 \times 10^{-10}\ e^{-3080/T}$	295
Jones & Davidson	47	$4 \times 10^{-11}\ e^{-2800/T}$	769 - 910
Kaufman	25	$1.4 \times 10^{-12}\ e^{-1500/T}$	Review
Phillips & Schiff	60	2.5×10^{-14}	298
Pshezhetskii et. al.	76	$3.83 \times 10^{-12}\ e^{-2500/T}$	303 - 443
Urbach, Zaslowsky et. al.	49,50	$7.1 \times 10^{-12}\ e^{-1600/T}$	273 - 353

3. Ionization

$N + O \rightarrow NO^+ + e$ $\qquad E = 2.76$ eV.

The reaction in the ion-electron recombination direction has been studied at room temperature by a number of workers including Weller (Ref. 80), Gunton (Ref. 81), Doering (Ref. 82), Young (Ref. 83), Van Lint (Ref. 84), and Bascombe (Ref. 85), over a temperature range at low temperatures by Gunton (Ref. 81); and at high temperatures by Stein (Ref. 86). The reaction in the ionization direction has been studied at high temperatures by Lin (Ref. 87). There have also been a number of analyses of atmospheric data, such as that of Donahue who made a complex analysis of atmospheric kinetics over a large altitude range.

The data given consideration here are shown in figure 17. Gunton obtained data at 196, 298, and 318 K creating the ions by photoionization with the ions being in low vibrational levels of the ground electronic state. The data of the several other investigators are in agreement with these data considering the uncertainties involved. Data are listed in Table VII.

At high temperatures, the data of the ionization reaction are weighed most heavily since that is the more important at such temperatures. It is, of course, possible that a different rate constant should be used when the ion-electron recombination reaction predominates from that used when the ionization reaction predominates. This is one way to allow for the effect of excited states - the combination into them and the non-Boltzmann distribution among the

states of the reactant. But, it would seem that a single rate constant would fit the data accurately enough. It is, therefore, suggested that the rate constant

$$k = 2.4 \times 10^{-3\pm.47} T^{-1.5}$$

be used for the recombination reaction and

$$k = 8.6 \times 10^{-13\pm0.5} e^{-31900/T}$$

be used for the ionization reaction. A factor of three is suggested for the uncertainty although it is certainly less at low temperatures.

Table VII. $NO^+ + e \rightarrow N + O$

Author	Ref	$k(cm^3\ particle^{-1}\ s^{-1}$	T(K)
Bascombe	85	2×10^{-7}	2000
Biondi	88	$4.7 \times 10^{-4} T^{-1.2}$	Review
Daiber	89	$6 \times 10^{-4} T^{-3/2}$	4900 - 7700
Doering	82	3×10^{-7} to 2×10^{-6}	300
Donahue	90	$5.2 \times 10^{-7} \left(\frac{T}{Tr}\right)^{-1.4}$	Tr = T (130 km)
Gunton	81	1.0×10^{-6} 4.6×10^{-7} 3.5×10^{-7}	196 298 358
Stein	86	4×10^{-8}	2900
Van Lint	84	3.7×10^{-7}	300
Weller	80	6×10^{-7}	300
Young	83	5×10^{-7}	300
$N + O \rightarrow NO^+ + e$			
Lin	87	$5 \times 10^{-11} T^{-1/2} e^{-32500/T}$	

4. Collisional Ionization

$N_2 + M \rightarrow N_2^+ + e + M$ $\quad M = N_2, O_2$ $\quad \Delta E = 15.58$ eV

$O_2 + M \rightarrow O_2^+ + e + M$ $\quad M = N_2, O_2$ $\quad \Delta E = 12.06$ eV

Before the shocked gas has had much opportunity to dissociate and hence to ionize by associative ionization, some appreciable ionization may occur by molecule-molecule collisions. This will only occur to a significant extent if the translational temperature is very high. Ionization of atoms by this mechanism will be unimportant since once appreciable numbers of atoms are available, associative ionization will occur and the temperature will have dropped enough to reduce collisional ionization probabilities drastically. The probability of molecular ionization will be greatest before any relaxation other than translational occurs, since then, the kinetic temperature is high. The only available data are for just such conditions. The data of Utterback and co-workers (Ref. 91), from a study of molecular beam colliding with molecules at room temperature, is of cross-sections for collisions with high kinetic energy with the molecules in the ground electronic state and almost entirely in the ground vibrational state. This is reasonably like the case of the earliest collisions in the shock layer. The data do not apply as well to the molecules once they have acquired significant vibrational energy, but no other data are available and its use is still the best approximation. Utterback has suggested that more appropriate data could be obtained by a complex reinterpretation of his data.

The data for an N_2 beam with O_2 target gas were essentially the same as for an O_2 beam with N_2 target gas. It was difficult to separate the formation of N_2^+ from that of O_2^+. Data below the N_2 ionization threshold is, of course, for the formation of O_2^+. Because of the distribution of energy of collisions, all of the data in the N_2 - O_2 system was attributed to O_2^+ formation although this is only for convenience. It introduces little error.

The rate constants obtained for the above reactions from Utterback's data are given in Table VIII. It should be noted that Utterback obtained no NO^+ from N_2 - O_2 collisions and his data should not be interpreted in that way. The rate constants given apply to a system with a Boltzmann distribution of kinetic energy and with the molecules in the ground electronic and mainly ground vibrational states.

It is practically impossible to assign an uncertainty for these rate constants. Sources of error include the data extrapolation to lower energies, the uncertainty and

spread in collision energy, the application to vibrationally excited states. The uncertainty is at least an order of magnitude and could more conservatively be given as two orders of magnitude. It is certainly greater at comparatively low temperatures and small at very high temperatures. Data were obtained from 20 to 500 ev.

It should be mentioned that ion-pair formation could be of some importance but data on this for the nitrogen-oxygen are lacking. However, the lack of any ions at the appropriate energies in Utterback's work indicates the process may not be significant.

Table VIII. Collisional Ionization Rates

$N_2 + N_2 \rightarrow N_2^+ + e + N_2$	$k = 3 \times 10^{-20 \pm 2} T^2 e^{-181000/T}$
$O_2 + N_2 \rightarrow O_2^+ + e + N_2$	$k = 1 \times 10^{-20 \pm 2} T^{1.5} e^{-140000/T}$
$O_2 + O_2 \rightarrow O_2^+ + e + O_2$	$k = 2 \times 10^{-20 \pm 2} T^{1.5} e^{-140000/T}$

Cross-section data are available for electron collision ionization. Again, these processes are most important for the very early times, before much relaxation has occurred. Thus, the data from electron beams passing through a stationary target gas are most appropriate since the only appreciable energy is the kinetic energy. There have been many studies on these two reactions. These data have been critically evaluated by Kieffer and Dunn (Ref. 91a,91b). In general, the agreement is very good among the various studies. For use here, data in the low-energy range of the study by Englander-Golden (Ref. 92) and of Tate (Ref. 93) have been used for N_2. The data on O_2 obtained in these same studies and that of Assundi (Ref. 94) have been used to obtain that rate constant. The rate constants so obtained are:

$N_2 + e \rightarrow N_2^+ + 2e$	$k = 5.3 \times 10^{-11 \pm 1} T^{0.5} e^{-181000/T}$
$O_2 + e \rightarrow O_2^+ + 2e$	$k = 2.2 \times 10^{-11 \pm 1} T^{0.5} e^{-140000/T}$

The major source of uncertainty here is probably the application of data obtained for unexcited molecules to a system when at least some vibrational excitation enters. Thus, before any vibrational relaxation, the uncertainties are less than a factor of two, but a larger factor is applicable when the excitation state is considered.

Rate constants for the ionization can also be obtained from those of the reverse three-body recombination process. Those reverse rate constants have been obtained by theory such as by the Thomson Theory. Dunn (Ref. 94a) has reviewed the various theories and presented rate constants for the Thomson Theory. These are:

$$k_r\ (N_2) = 6.1 \times 10^{-22}\ T^{-2.5}$$

$$k_r\ (O_2) = 2.4 \times 10^{-21}\ T^{-2.5}$$

From these and the equilibrium constants, the ionization rate constants are:

$$k_i\ (N_2) = 5.9 \times 10^{-6}\ T^{-1}\ e^{-181000/T}$$

$$k_i\ (O_2) = 1.5 \times 10^{-5}\ T^{-1}\ e^{-140000/T}$$

These are obviously much different from the rate constants from the electron collision data. Since those from ionization are more applicable until the electronic excitation reaches a distribution nearing that corresponding to the kinetic temperature, it is suggested that the first set be used for the early ionization. The use of the recombination rate constant obtained from the theory would be advisable when the recombination step is important but the three-body recombination probably does not compete with dissociative recombination ($XY^+ + e \rightarrow X + Y$) for conditions of interest here. Therefore, the use of the rate constants from electron collision ionization cross-section data is advised.

5. Electron Attachment and Detachment

$O_2 + e + M \rightarrow O_2^- + M$ $\qquad\qquad \Delta E = 0.43$ eV

The three-body attachment of electrons to O_2 has been most thoroughly studied by Phelps and co-workers. The attachment is fast with O_2 and certain other less-abundant species as collision partners and relatively slow with N_2 as the third-body. Phelps (Ref. 102) has recently reviewed the data on this reaction and has suggested the values

M	k (cm^6 particle^{-2} s^{-1})
O_2	$(4.2 \pm 0.6) \times 10^{-27} T^{-1} e^{-600/T}$
N_2	$(1 \pm 0.5) \times 10^{-31}$
CO_2	$(3.3 \pm 0.7) \times 10^{-30}$
H_2O	$(1.4 \pm 0.2) \times 10^{-29}$

The data of Chanin, Phelps and Biondi (Ref. 103) and of Pack and Phelps (Ref. 104), most heavily relied upon, were obtained in a drift tube system in which the electrons were found to be thermalized with average energies of .023 to 1 ev, the distribution being different from any standard distribution. The gas temperatures were varied from 195 to 583 K and these data were used at average electron energies of the corresponding temperature. Other data (Ref. 105-108) at or near 300 K agreed well with these data for O_2 and N_2. The three-body collision may be either a two-body formation of O_2^- in an excited form which is subsequently stabilized by a collision or a two-body formation of an O_4 complex which then undergoes dissociative attachment in a collision with an electron. The data may be for either of these or possibly a combination of them. At higher temperatures there are few data. Chatterton and Craggs (Ref. 169) have obtained data for average electron energies of 0.6 to 1.1 ev. The values fall about a factor of three above the extrapolated curve of Phelps. However, the gas temperatures are low so that the mechanism of O_2^- formation, the possible occurrence of excited states, the conversion of kinetic energy, and any other uncertainties inherent in the non-thermalization of their system are involved.

Since at high temperatures the rapid detachment makes the attachment of little importance, the extrapolated curve is suitable for use. Therefore, a rate constant of $4.2 \times 10^{-27} \pm .1\ T^{-1} e^{-600/T}$ is suggested for O_2 as the third-body and $1 \times 10^{-31} \pm .3$ for N_2. Other collision partners are unimportant because of low rates and competing reactions.

It is concluded that the values suggested by Phelps are the most suitable numbers for use here, being reasonably accurate for the temperature range of interest.

$O_2^- + O \rightarrow O_3 + e$ $\qquad \Delta E = -0.62$ eV

Fehsenfeld and coworkers (Ref. 110,111) have the only reliable data on this reaction. They report a value of 2.5×10^{-10}, this being a slight revision of previously reported

values (Ref. 112). No temperature dependence is given. The uncertainty is estimated as not more than a factor of two.

Curran's data (Ref. 113) could be used to obtain a temperature dependence, the shape of the cross-section curve indicating a variation of T^1 or $T^{3/2}$. However, the threshold shown by these data is in considerable error (about .4 instead of .6 ev), so that the data do not seem suitable for use.

A value of $2.5 \times 10^{-(10 \pm 0.5)}$

is suggested and nothing can be said about the temperature dependence.

$O_3 + e \rightarrow O^- + O_2$ $\Delta E = -0.43$ eV

For this reaction the only reliable data are from the work of Fehsenfeld and co-workers (Ref. 110). Their latest published value is 4×10^{-11} cm^3 $particle^{-1}$ s^{-1}. Limits of the uncertainty are given as 10^{-11} to 10^{-10}. Data were obtained at only room temperature, 300 K. Curran (Ref. 113) gives some cross-section data but there is a question about these data. They have been used to obtain a temperature dependence of $T^{1.75}$. This, with Fehsenfeld's value, would give a rate constant of $4 \times 10^{-11} \left(\frac{T}{300}\right)^{1.75}$ or $1.85 \times 10^{-15} T^{1.75}$, but it is thought that the data and this temperature dependence are both suspect. It is probably better to use no temperature dependence at this time. Thus a rate constant of $4 \times 10^{-(11 \pm 0.5)}$ is recommended with no meaningful temperature dependence information.

Using the equilibrium constant, $K = 1.67 \times 10^{-10} T^{0.83} e^{-4700/T}$ obtained from data in the JANAF tables (Ref. 48), the rate constant for the reverse reaction is $6.7 \times 10^{-21 \pm .5} T^{.83} e^{-4700/T}$.

6. Negative Ion Charge Exchange Reactions

The reactions of this type which are of possible importance are:

$$O_2^- + O \rightarrow O_2 + O^-$$
$$O_2^- + O_3 \rightarrow O_2 + O_3^-$$
$$O^- + O_3 \rightarrow O + O_3^-$$
$$O^- + O_3 \rightarrow O_2^- + O_2$$
$$O_2^- + N \rightarrow O^- + NO$$

$$O_2^- + NO \rightarrow NO_2^- + O$$

$$O_3^- + O \rightarrow O_2^- + O_2$$

$$O_3^- + CO_2 \rightarrow CO_3^- + O_2$$

$$O_3^- + NO \rightarrow NO_3^- + O$$

$$NO_3^- + O \rightarrow NO_2^- + O_2$$

$$CO_3^- + O \rightarrow O_2^- + CO_2$$

The data on these reactions are limited. There are room temperature data on several of them, mainly from the work of Ferguson et al. In addition, there are data at energies of several eV and above, some of which are on the reverse reaction.

For the $O_2^- + O_3 \rightarrow O_2 + O_3^-$ Fehsenfeld (Ref. 110-112) gives a value of 3×10^{-10}. This is the only usable value for this. The temperature dependence is unknown and it is best to assume none. Since, because of electron detachment from O_2^-, the reaction is unimportant at high temperatures, the temperature dependence is of little consequence. A rate constant of $3.0 \times 10^{-10} \pm .3$ is recommended.

The reaction $O_2^- + O \rightarrow O_2 + O^-$ competes with the associative detachment reaction $O_2^- + O \rightarrow O_3 + e$, both in the wake and in the laboratory system. Its influence is thereby limited. This also makes it difficult to obtain a value of the rate constant. Fehsenfeld et al (Ref. 112) have obtained a combined rate constant for the two reactions of 5×10^{-10} cm^3 $particle^{-1}$ s^{-1}. He later (Ref. 110) gave a rate constant of 3.3×10^{-10} for the associative detachment but the difference in this and the previous value should not be attributed to the charge transfer but rather to a more accurate and lower total value for the two reactions. Still more recently, Ferguson (Ref. 111) gives a value of 2.5×10^{-10}. There are no data which can be attributed directly to the change transfer reaction. It is now thought by Ferguson (Ref. 114) that the charge transfer is slower than the associative detachment so that its influence on the O_2^- or O concentration is relatively unimportant. It may be of some importance to the O^- concentration and in this way affect the electron density.

The reverse attachment reaction has been studied at energies above the endothermicity (0.62) by Paulson (Ref. 115). By extrapolating this, integrating for a Maxwellian

distribution, and using the equilibrium constant a rate constant of $3 \times 10^{-14} T^{1/2}$ can be obtained. This would be 6×10^{-13} at 300 K. It is probable that such an extrapolation is not reasonable although it is only from 4 eV down to 3.7 eV. It is interesting to note that he finds the charge transfer reaction to be three times as fast as the charged rearrangement giving the same products.

Woo, Branscomb, and Beaty (Ref. 116) obtained rate constants at elevated temperatures for the endothermic reaction. Use of the data would give much too low an endothermicity and they concluded that their distribution was non-Maxwellian and unknown and these data cannot be used.

With this limited information, a reasonable rate constant is 1×10^{-11} $^{+1}_{-3}$. No temperature dependence will be used since at higher temperatures O_2^- will be unimportant.

The reactants $O^- + O_3$ can form $O + O_3^-$, $O_2^- + O_2$, or $O_2 + O_2 + e$ by exothermic reactions. The charge transfer reaction giving the first of these sets of products is apparently the fastest. Fehsenfeld (Ref. 110) found a rate constant of 7.0×10^{-28} cm^3 particle^{-1} s^{-1}.

The reaction $O_2^- + NO \rightarrow O + NO_2^-$ has evidently not been studied. If large concentrations of NO persist in parts of the wake where attachment has become important, data on this can well be important.

7. Ion-Pair Neutralization

$X^+ + Y^- \rightarrow X + Y$

Data on ion-ion neutralization are very limited. However, because this is a major mechanism for the removal of both positive and negative ions and hence appreciably affect the electron density it should be included here. It should be noted that the simple mechanism noted is not necessarily that which occurs. If the positive ion is diatomic (or larger) it may well dissociate (Ref. 117) since the exothermicity is great enough, i.e. $XZ^+ + Y^- \rightarrow X + Z + Y$. A three-body process, e.g. $X^+ + Y^- + M \rightarrow X + Y + M$ (or various other products), may be important. The information on the ion-ion recombination has been reviewed recently by Biondi (Ref. 88). The rate constants suggested there are listed in Table IX. The same rate constants are given for all ions since no data are available to determine different ones for different ions. Theory does provide distinctions for different species in the three-body ion-ion recombination.

Thus for the more important reactions involving negative ions, the following rate constants are suggested:

Table IX. Rate Constants for Reactions Involving Negative Ions

	$k(cm^3\ particle^{-1}\ s^{-1})$
$O_2 + e + O_2 \rightarrow O_2^- + O_2$	$4.2 \times 10^{-27} \pm .1\ T^{-1}\ e^{-600/T}$
$O_2 + e + N_2 \rightarrow O_2^- + N_2$	$1 \times 10^{-31} \pm .3$
$O_2^- + O_3 \rightarrow O_2 + O_3^-$	$3 \times 10^{-10} \pm .3\ (\frac{T}{300})\quad 0 \pm 1$
$O_2^- + O \rightarrow O_3 + e$	$2.5 \times 10^{-10} \pm .5$
$O_3 + e \rightarrow O^- + O_2$	$4 \times 10^{-11} \pm .5$
$X^+ + Y^- \rightarrow X + Y$	$6 \times 10^{-5} \pm .5\ T^{-1}$
$X^+ + Y^- + M \rightarrow X + Y + M$	$3 \times 10^{-19} \pm .5\ T^{-2.5}$

The most stable negative ion will probably only disappear by ion-ion recombination. The most stable negative ions are probably CO_3^- and NO_3^-. These are formed directly from O_3^- by charged rearrangement reactions. If it is desired to simplify the chemical system by omitting CO_3^- and NO_3^-, the conversion of O_3^- to a less stable negative ion by $O_3^- + O \rightarrow O_2^- + O_2$ may be included with a pseudo rate constant reduced by multiplying it by the fraction taking that path, i.e.

$$k^{\text{pseudo}}_{(O_3^- + O)} = \frac{k^{\text{true}}_{(O_3^- + O)}\ N_O}{k^{\text{true}}_{(O_3^- + O)} N_O + k_{(O_3 + CO_2)} N_{CO_2} + k_{(O_3 + NO)}\ N_{NO}}$$

Other terms may be included in the denominator which convert O_3^- to other negative ions which in turn are stable or convert to CO_3^- or NO_3^-. This pseudo rate constant would then have to be calculated at each iteration. If the $O_3^- + O$ reaction is negligible, the O_3^- can be regarded as the final negative ion and it may be taken as disappearing only by ion-ion recombination.

8. Positive Ion Charge Exchange Reactions

There are more than twenty exothermic reactions in the nitrogen-oxygen system which could logically be expected to change the identity of the positive ions in the re-entry flow field. Consideration of all of these indicates that those which are important and have most effect on the flow field are:

$$N_2^+ + O_2 \rightarrow N_2 + O_2^+$$

$$N_2^+ + NO \rightarrow N_2 + NO^+$$

$$N_2^+ + O \rightarrow NO^+ + N$$

$$O_2^+ + NO \rightarrow O_2 + NO^+$$

Data are given in table X. All of these studies were carried out at about 300 K. No usable information is available on temperature dependence. Hence, the factors suggested for uncertainty hold only for room temperature. At high temperatures, these may be orders of magnitude in error. This is expressed as an uncertainty in the temperature dependence of $(\frac{T}{300})^{\pm 1.5}$ where the exponent 1.5 is merely an estimate.

$N_2^+ + O_2 \rightarrow N_2 + O_2^+$

Several investigations of this reaction are in good agreement. Fite (Ref. 95), in a stationary afterglow obtained a value of 2×10^{-10} while Fehsenfeld (Ref. 96) and co-workers and Warneck (Ref. 97), in flowing afterglows, obtained 1×10^{-10} and 1.1×10^{-10} respectively. Fehsenfeid's value will be accepted here with a factor of two uncertainties at room temperature, i.e. $k = 1 \times 10^{-10 \pm .3}$.

$N_2^+ + NO \rightarrow N_2 + NO^+$

The results of Ferguson (Ref. 98) et. al. and of Warneck (Ref. 97) are in excellent agreement (5×10^{-10} and 4.8×10^{-10}). The value of 5×10^{-10} with an uncertainty of a factor of two at 300 K is suggested here, i.e. $5 \times 10^{-10 \pm .3}$.

$N_2^+ + O \rightarrow NO^+ + N$

The only available data is that of Ferguson (Ref. 99) et. al. This value of 2.5×10^{-10} at 300 K is acceptable but probably has somewhat more uncertainty than the others since atomic oxygen is involved. A factor of five uncertainty is suggested. Thus, $k = 2.5 \times 10^{-10} \pm .7$.

$O_2^+ + NO \rightarrow O_2 + NO^+$

The results of Ferguson (Ref. 98) and co-workers and of Warneck (Ref. 97) are again in excellent agreement (8×10^{-10} and 7.7×10^{-10}). The value of 8×10^{-10} with an uncertainty of a factor of two is suggested, i.e. $8 \times 10^{-10} \pm .3$

Table X. $N_2^+ + O_2 \rightarrow N_2 + O_2^+$

Author	Ref.	$k(cm^3\ particle^{-1}\ s^{-1})$	TK
Fite et. al.	95	2×10^{-10}	300K
Fehsenfeld et. al.	96	1×10^{-10}	300K
Warneck	97	1.1×10^{-10}	300K
Poppoff	100	2×10^{-10}	(E Region)
Aquilanti & Volpi	101	6.5×10^{-11}	300K
$N_2^+ + NO \rightarrow N_2 + NO^+$			
Ferguson et. al.	98	5×10^{-10}	300K
Warneck	97	4.8×10^{-10}	300K
$N_2^+ + O \rightarrow NO^+ + N$			
Ferguson et. al.	99	2.5×10^{-10}	300K
$O_2^+ + NO \rightarrow O_2 + NO^+$			
Ferguson	98	8×10^{-10}	300K
Warneck	97	7.7×10^{-10}	300K

$CO_2 + M \rightarrow CO + O + M$ $\Delta E = 5.45$ eV

The dissociation of carbon dioxide has been studied by Steinberg (Ref. 120), by Brabbs (Ref. 121) and by Davies (Ref. 122). Data are shown in figure 18. Very different rate expressions are obtained by the three workers. These investigators each fit their data with an activation energy much lower than the endothermicity. The higher the temperatures of the studies, the lower the determined activation energy. It appears that the major dissociation is from the upper vibrational levels which are nearly in equilibrium with the dissociation products, CO and O. It is chosen here to consider the data of Steinberg and of Davies more than that of Brabbs since the last is at a lower temperature range than that of major interest and because of the method of analysis employed therein. The data can then be fit reasonably well by an expression employing the endothermicity although the use of this as the activation energy is only for convenience. This is also a compromise since the individual studies indicate a lower value, the composite of all the studies indicate a higher value. Thus, a suggested rate constant is:

$$k_d\ (N_2) = 1.8 \times 10^8\ T^{-4.5}\ e^{-63800/T}$$

for N_2 as the collision partner while for Ar, the suggested value is

$$k_d\ (Ar) = 1.6 \times 10^8\ T^{-4.5}\ e^{-63800/T}$$

No attempt has been made to consider or include the data from the reverse reaction. These data vary widely, probably bear little relation to the dissociation reaction, and are difficult to interpret.

Table XI. Suggested Rate Constants $(k = a\ T^b\ e^{-c/T})$ *#

	Forward			Reverse		
$O_2 + M \rightarrow O + O + M$	a	b	c	a	b	c
$M = O_2$	1.37(-5±.5)	-.83	59400	1.9(-32±.5)	-.33	0
O	1.5(-4±.7)	-1	59400	2.1(-31±.7)	-.5	0
N_2	2.2(3±.7)	-1.7	59400	3.0(-30±.7)	-1.2	0
N, NO, Ar	2.4(-3±.5)	-1.8	59400	3.3(-30±.5)	-1.3	0

	Forward			Reverse		
$N_2 + M \rightarrow N + N + M$	a	b	c	a	b	c
$M = N_2$	$8.3(-6\pm.5)$	-.75	113200	$7.7(-31\pm.5)$	-.75	0
N	$5.0(-2\pm.6)$	-1.5	113200	$4.6(-27\pm.6)$	-1.5	0
O_2, O, NO, Ar	$4.8(-6\pm.5)$	-.82	113200	$4.4(-31\pm.5)$	-.82	0
$NO + M \rightarrow N + O + M$						
$M = NO, O, N$	$1.32(-2\pm.6)$	-1.5	75400	$9.1(-26\pm.6)$	-1.5	0
O_2, N_2	$1.5(-9\pm.5)$	0	75400	$1.1(-32\pm.5)$	0	0
Ar	$3.5(-8\pm.5)$	-.6	75400	$2.4(-31\pm.5)$	-.6	0
$O_3 + M \rightarrow O + O_2 + M$						
$M = N_2$	$2.1(-5\pm.6)$	-1.35	12300	$4.5(-29\pm.6)$	-2.0	0
O_2, N, O, NO	$2.3(-5\pm.6)$	-1.35	12300	$4.8(-29\pm.6)$	-2.0	0
Ar	$1.4(-5\pm.6)$	-1.35	12300	$2.9(-29\pm.6)$	-2.0	0
$O + N_2 \rightarrow N + NO$	$1(-10\pm.3)$	0	38000	$2.2(-11\pm.3)$	0	0
$O + NO \rightarrow N + O_2$	$7.2(-17\pm.3)$	1.5	19100	$3.0(-16\pm.3)$	1.5	3000
$O_2 + O_2 \rightarrow O + O_3$	$2.9(-11\pm.7)$	0	50190	$3.6(-11\pm.7)$	0	2750
$N + O \rightarrow NO^+ + e$	$8.6(-13\pm.5)$	0	31900	$2.4(-3\pm.5)$	-1.5	0
$N_2 + M \rightarrow N_2^+ + e + M$						
$M = N_2$	$3.0(-20\pm2)$	2.0	181000	$3.0(-36\pm2)$	0.5	0
e	$5.3(-11\pm1)$	0.5	181000	$5.3(-27\pm1)$	-1	0 (see text)
$O_2 + M \rightarrow O_2^+ + e + M$						
$M = N_2$	$1.0(-20\pm2)$	1.5	140000	$1.6(-36\pm2)$	0	0
O_2	$2.0(-20\pm2)$	1.5	140000	$3.2(-36\pm2$	0	0
e	$2.2(-11\pm1)$	0.5	140000	$3.5(-27\pm1)$	-1	0 (see text)
$O_2 + e + M \rightarrow O_2^- + M$						
$M = O_2$	$4.2(-27\pm.3)$	-1.0	600	$1.2(-11\pm.3)$	0.5	5700
N_2	$1(-21\pm.3)$	0	0	$3(-16\pm.3)$	1.5	5700

	Forward			Reverse		
	a	b	c	a	b	c
$O_2^- + O_3 \rightarrow O_2^- + O_3^-$	3(-10±.3)	T/300	0	3(-10±.3)	0	2800
$O_2^- + O \rightarrow O_3 + e$	2.5(-10±.5)	T/300	0	2.5(-9±.5)	0	7200
$O_3 + e \rightarrow O^- + O_2$	4(-11±.5)	T/300	0	6.7(-21±.5)	.83	4700
$X^+ + Y^- \rightarrow X + Y$	6(-5±.5)	-1	0			
$X^+ + Y^- + M \rightarrow X + Y + M$	3(-19±.5)	-2.5	0			
$N_2^+ + O_2 \rightarrow N_2 + O_2^+$	1(-10±.3)	T/300	0	3(-11±.3)	0	40900
$N_2^+ + NO \rightarrow N_2 + NO^+$	5(-10±.3)	T/300	0	1.5(-9±.3)	0	73100
$N_2^+ + O \rightarrow NO^+ + N$	2.5(-10±.7)	T/300	0	4.5(-10±.7)	0	35400
$O_2^+ + NO \rightarrow O_2 + NO^+$	8(-10±.3)	T/300	0	4.2(-10±.3)	0	32200

*Rate constants are in units to be used with concentrations in particles cm^{-3} and time in seconds. The number in parenthesis are the powers of ten by which the preceeding figure is to be multiplied.

For the exothermic reaction rate constants, the data cited are intended for general use in the temperature range of app. 100-5000 K.F or the endothermic reaction rate constants the data cited are intended for general use between temperatures of app. 1500-10,090 K. Individual exceptions to the above are discussed in the text.

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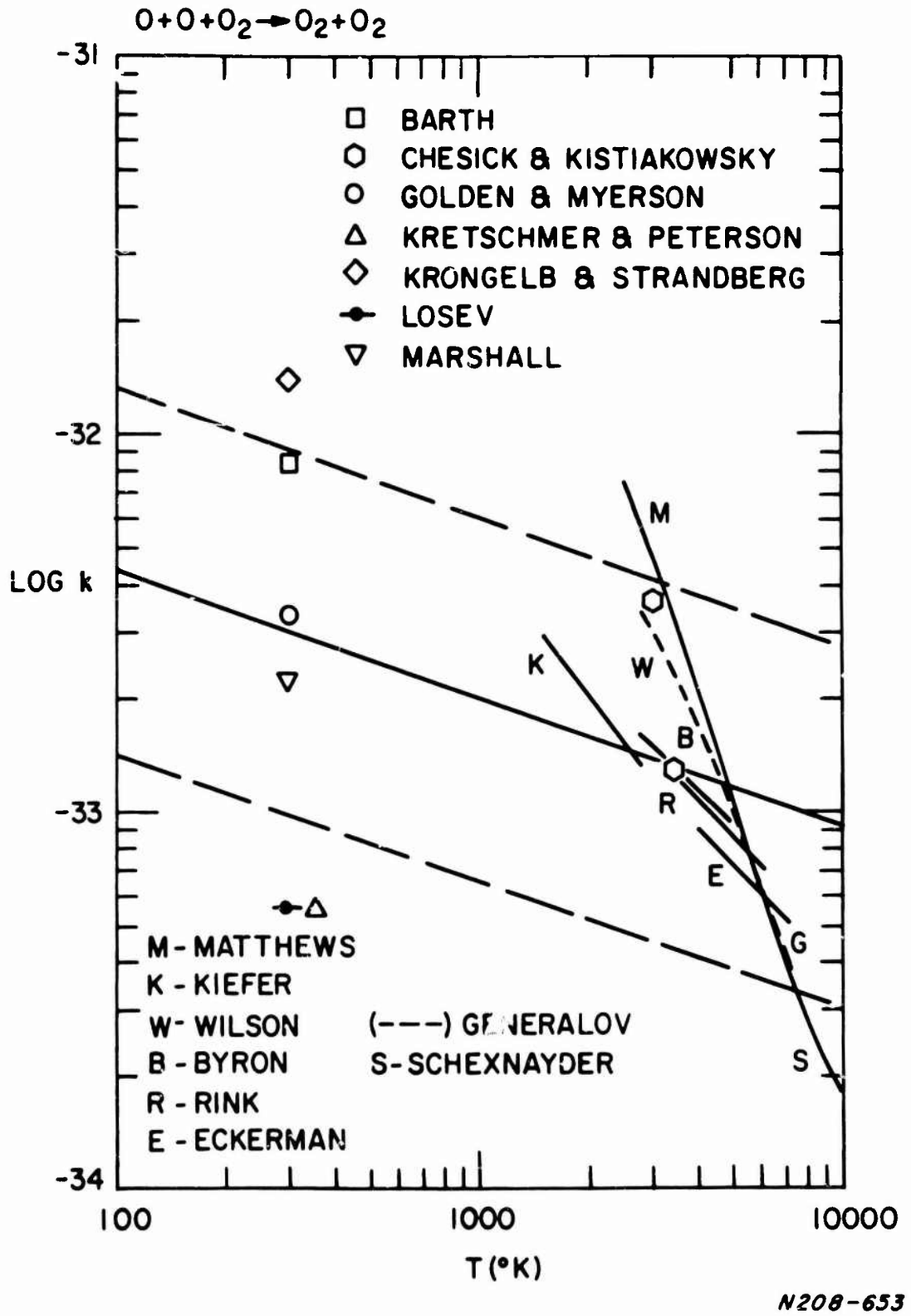

O+O+O2→O2+O2
-31
-32
-33
-34
LOG k
BARTH
CHESICK & KISTIAKOWSKY
GOLDEN & MYERSON
KRETSCHMER & PETERSON
KRONGELB & STRANDBERG
LOSEV
MARSHALL
M
K
W
B
R
E
G
S
M - MATTHEWS
K - KIEFER
W - WILSON
B - BYRON
R - RINK
E - ECKERMAN
(---) GENERALOV
S - SCHEXNAYDER
100
1000
10000
T(°K)
N208-653

Figure 1

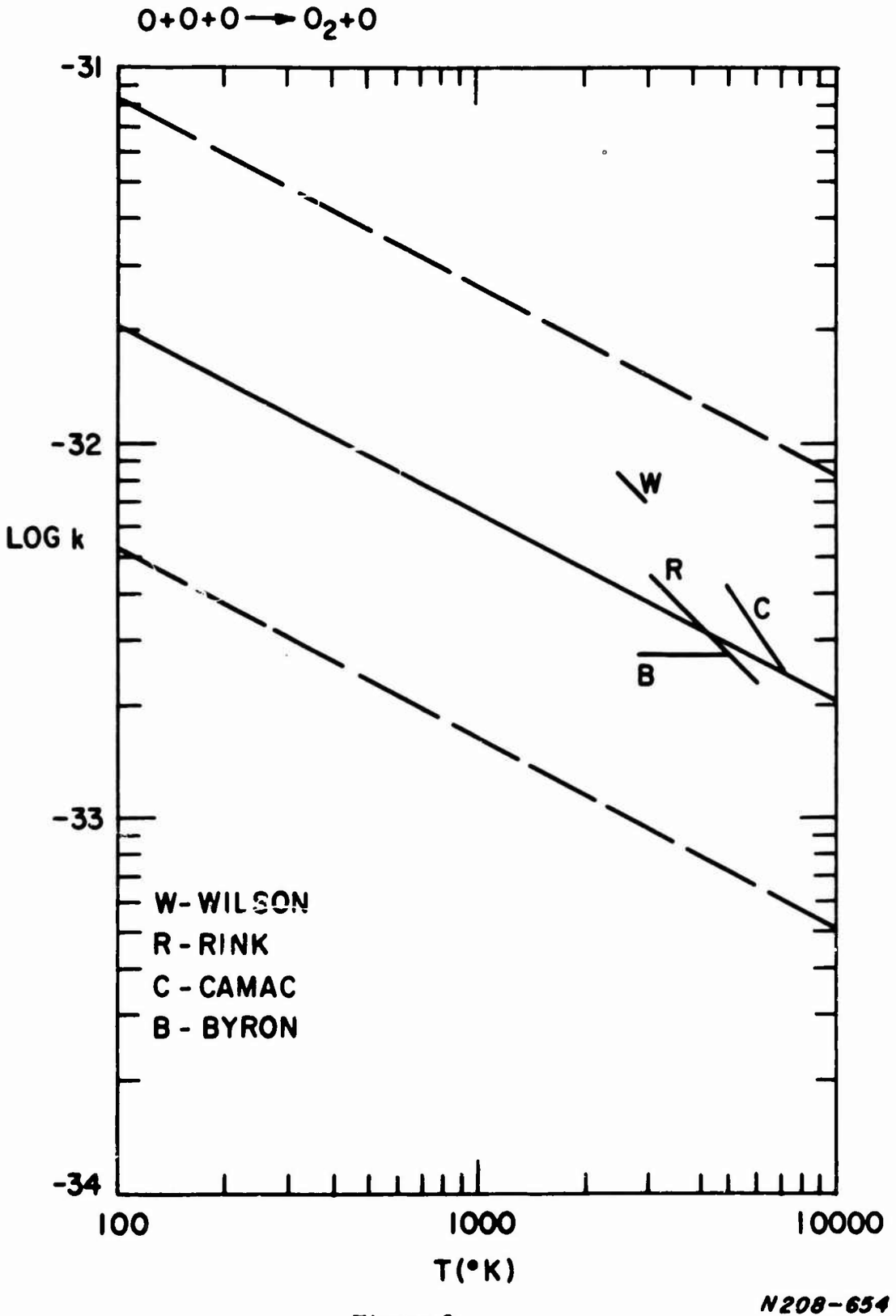

O+O+O → O2+O
-31
-32
-33
-34
LOG k
W
R
C
B
W- WILSON
R - RINK
C - CAMAC
B - BYRON
100
1000
10000
T(°K)
N208-654

Figure 2

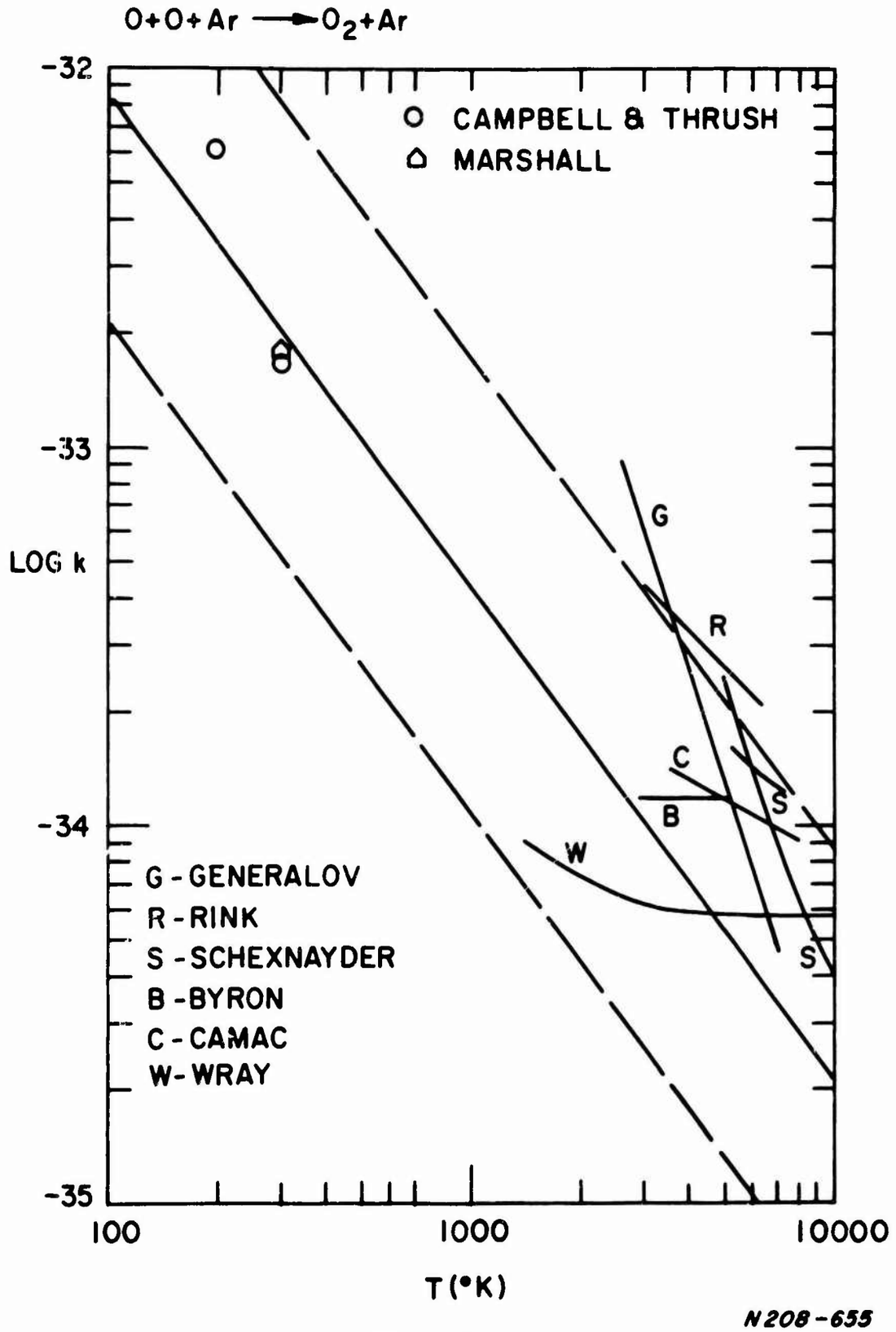

O+O+Ar ⟶ O2+Ar
-32
-33
-34
-35
LOG k
100
1000
10000
T(°K)
O CAMPBELL & THRUSH
Δ MARSHALL
G
R
C
B
S
W
S
G - GENERALOV
R - RINK
S - SCHEXNAYDER
B - BYRON
C - CAMAC
W - WRAY
N208-655

Figure 3

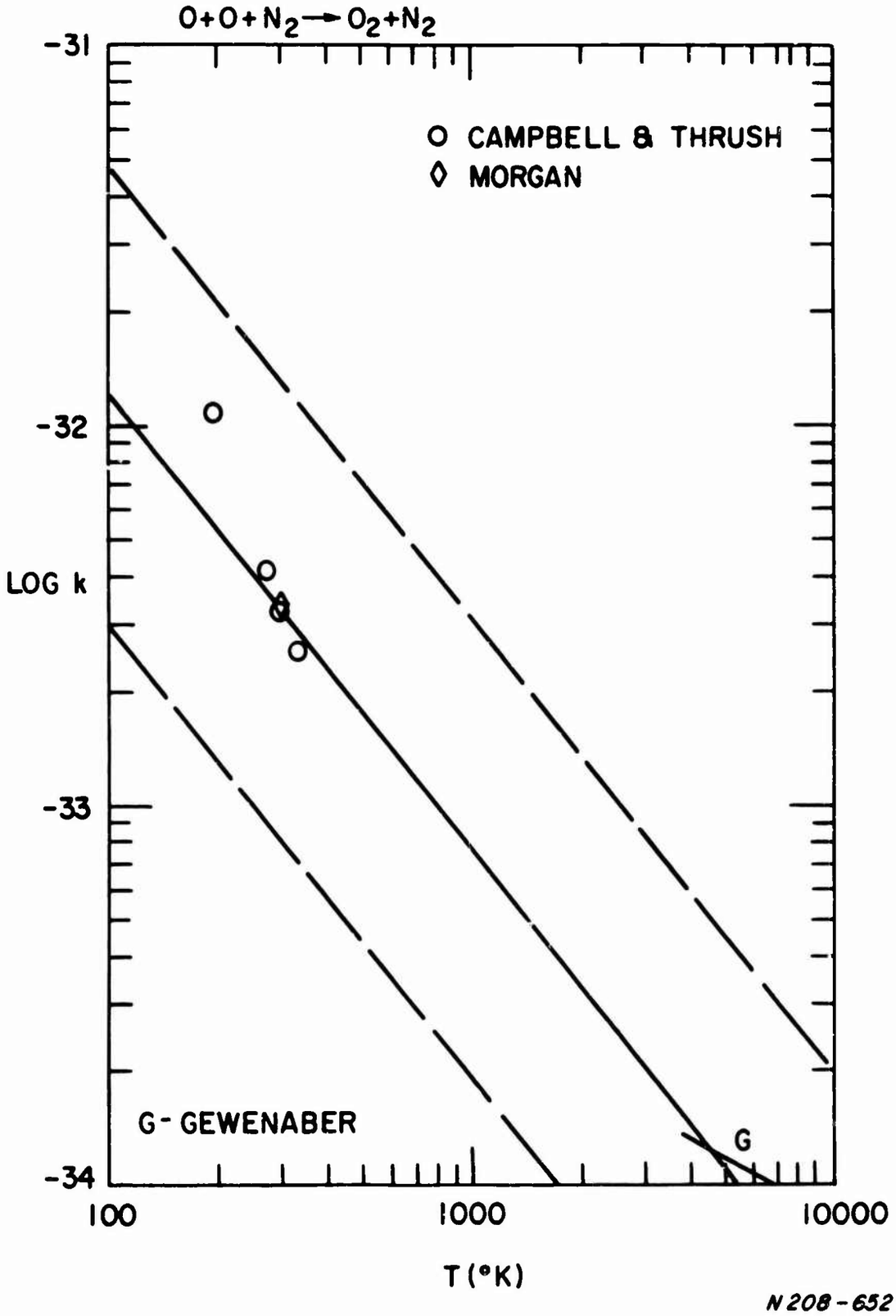

O+O+N2→O2+N2
-31
-32
-33
-34
LOG k
O CAMPBELL & THRUSH
◊ MORGAN
G- GEWENABER
G
100
1000
10000
T(°K)
N208-652

Figure 4

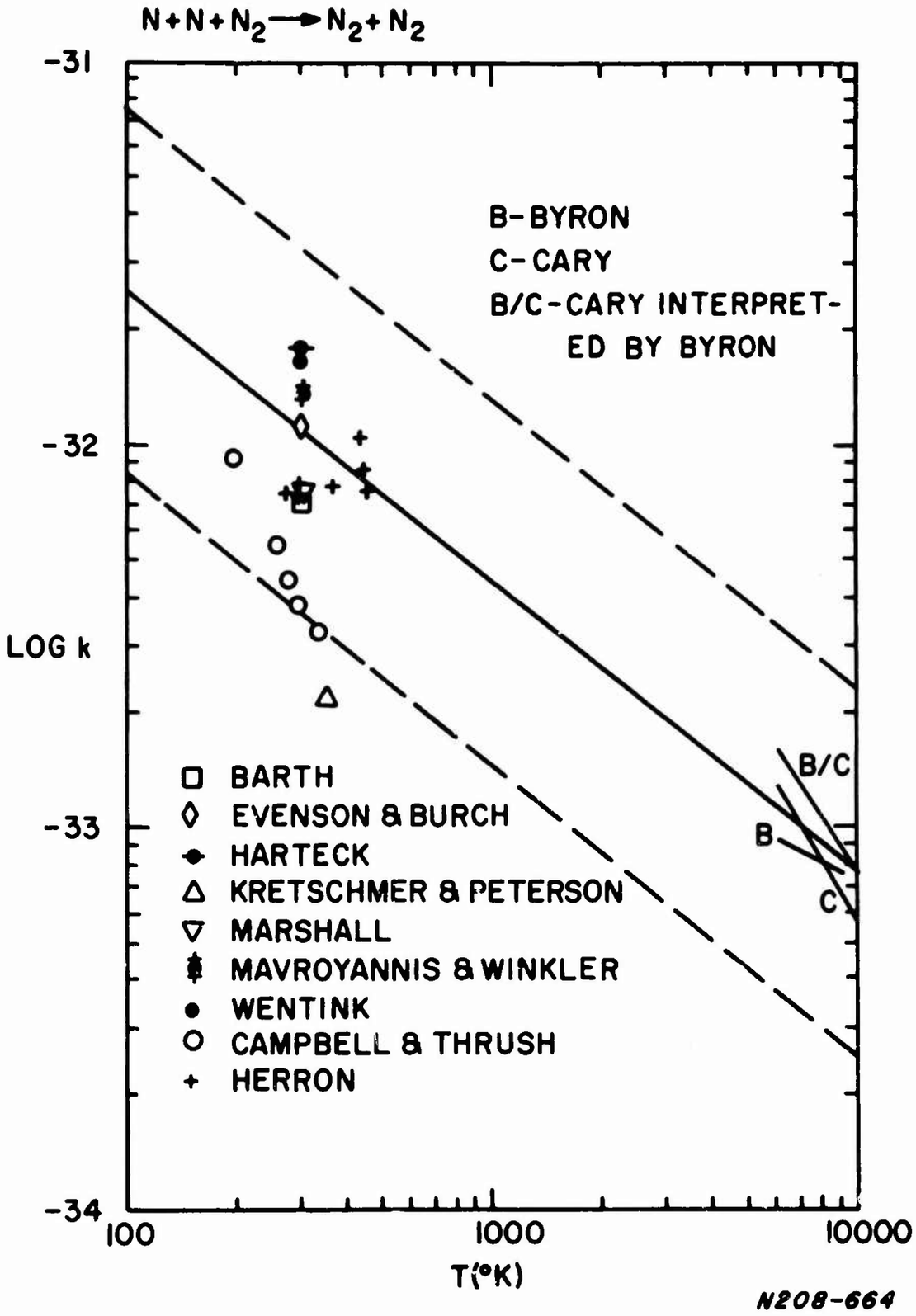

N+N+N2 → N2+N2
-31
-32
-33
-34
LOG k
100
1000
10000
T(°K)
B-BYRON
C-CARY
B/C-CARY INTERPRETED BY BYRON
B/C
B
C
BARTH
EVENSON & BURCH
HARTECK
KRETSCHMER & PETERSON
MARSHALL
MAVROYANNIS & WINKLER
WENTINK
CAMPBELL & THRUSH
HERRON
N208-664

Figure 5

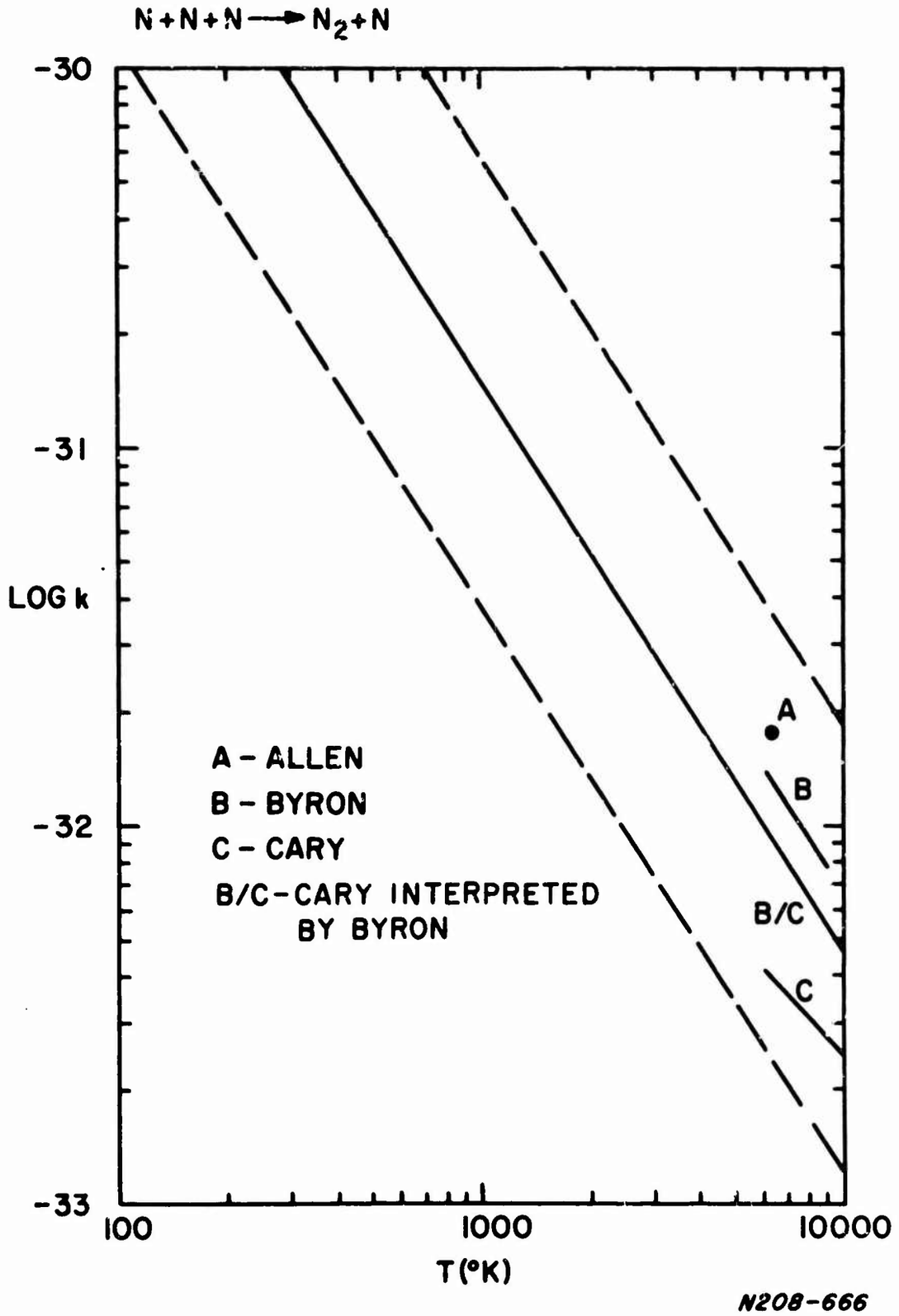

N+N+N → N2+N
-30
-31
-32
-33
LOG k
100
1000
10000
T(°K)
A - ALLEN
B - BYRON
C - CARY
B/C - CARY INTERPRETED BY BYRON
A
B
B/C
C
N208-666

Figure 6

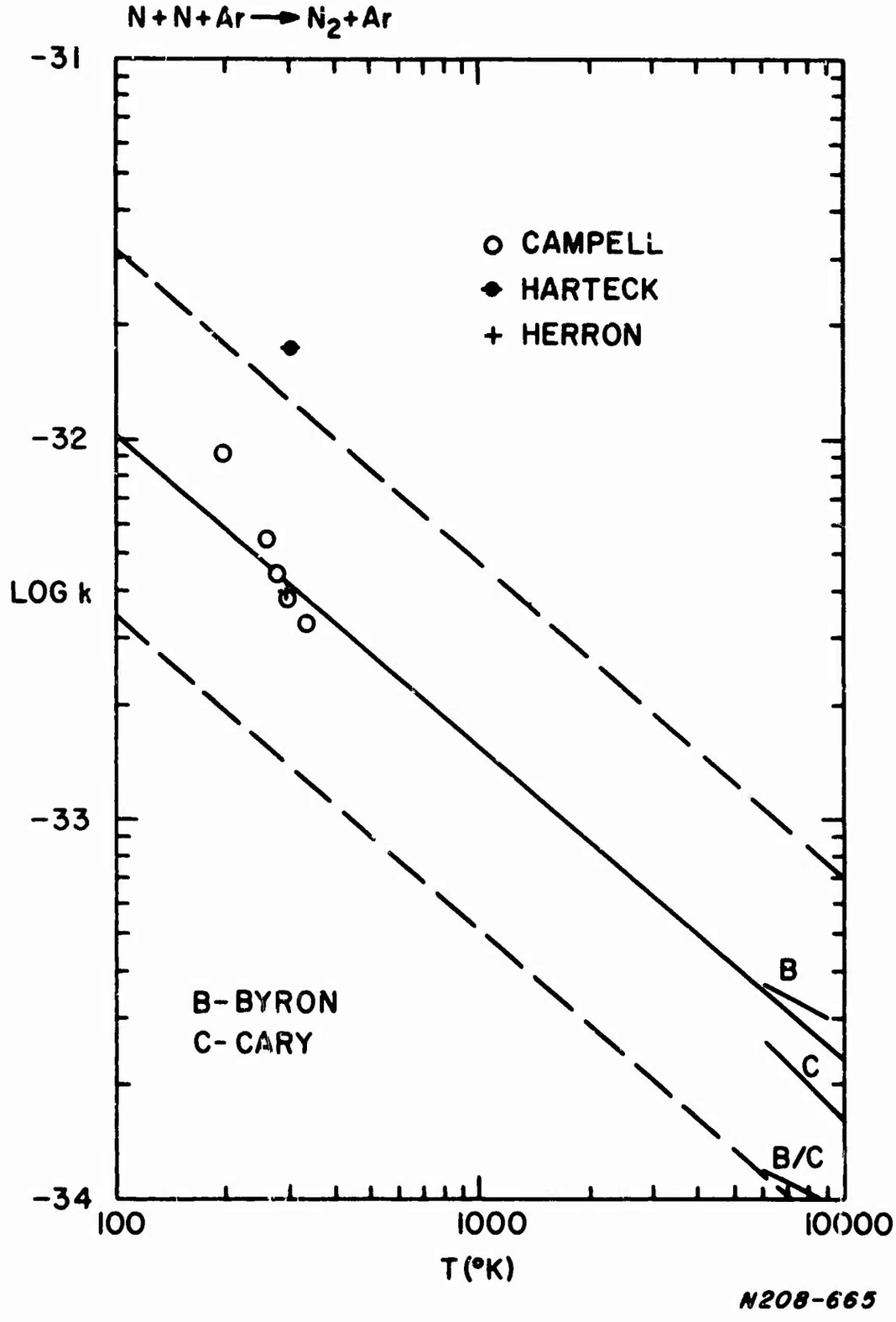

N+N+Ar → N2+Ar
-31
-32
-33
-34
LOG k
100
1000
10000
T(°K)
CAMPELL
HARTECK
HERRON
B
C
B/C
B-BYRON
C-CARY
N208-665

Figure 7

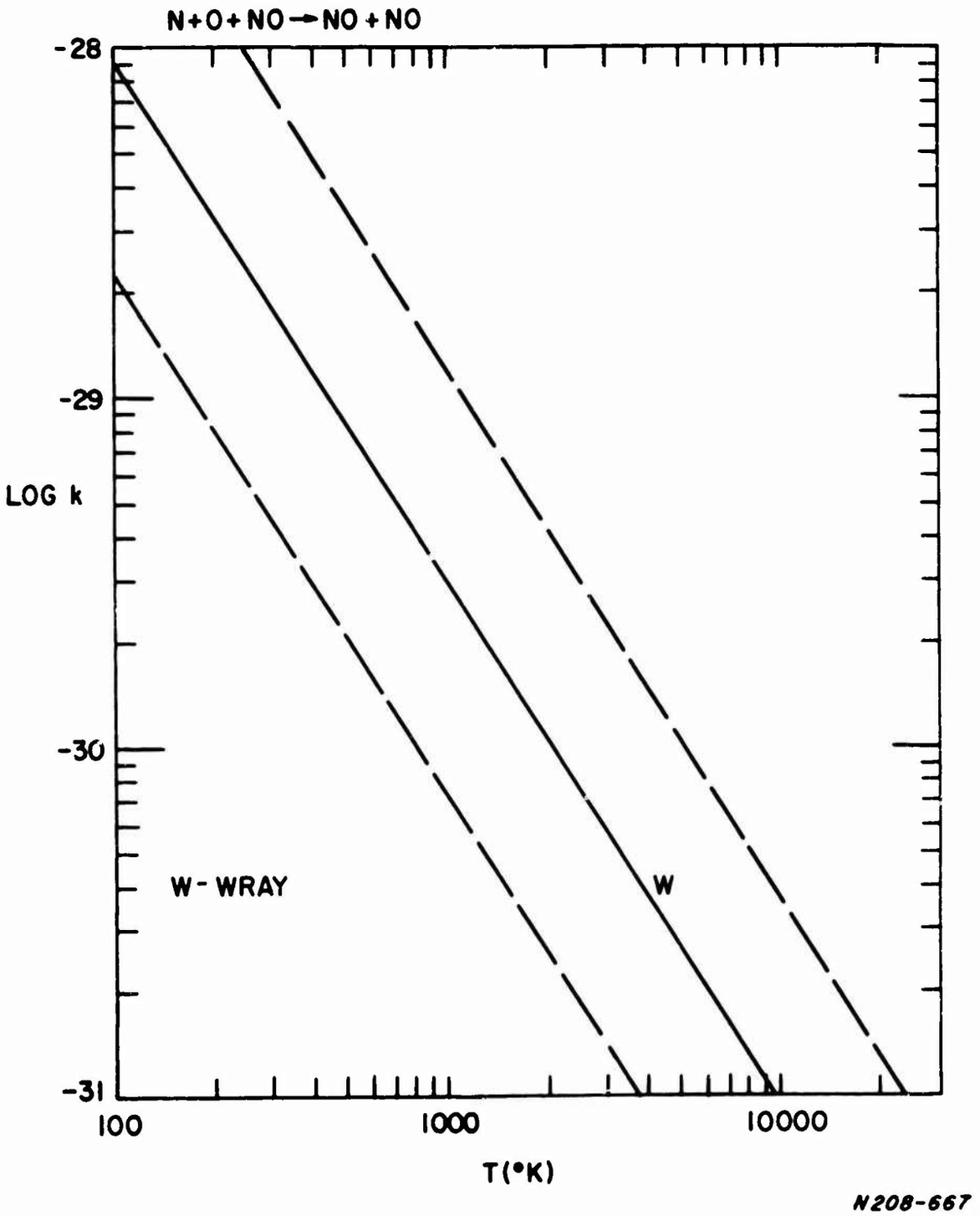


Figure 8

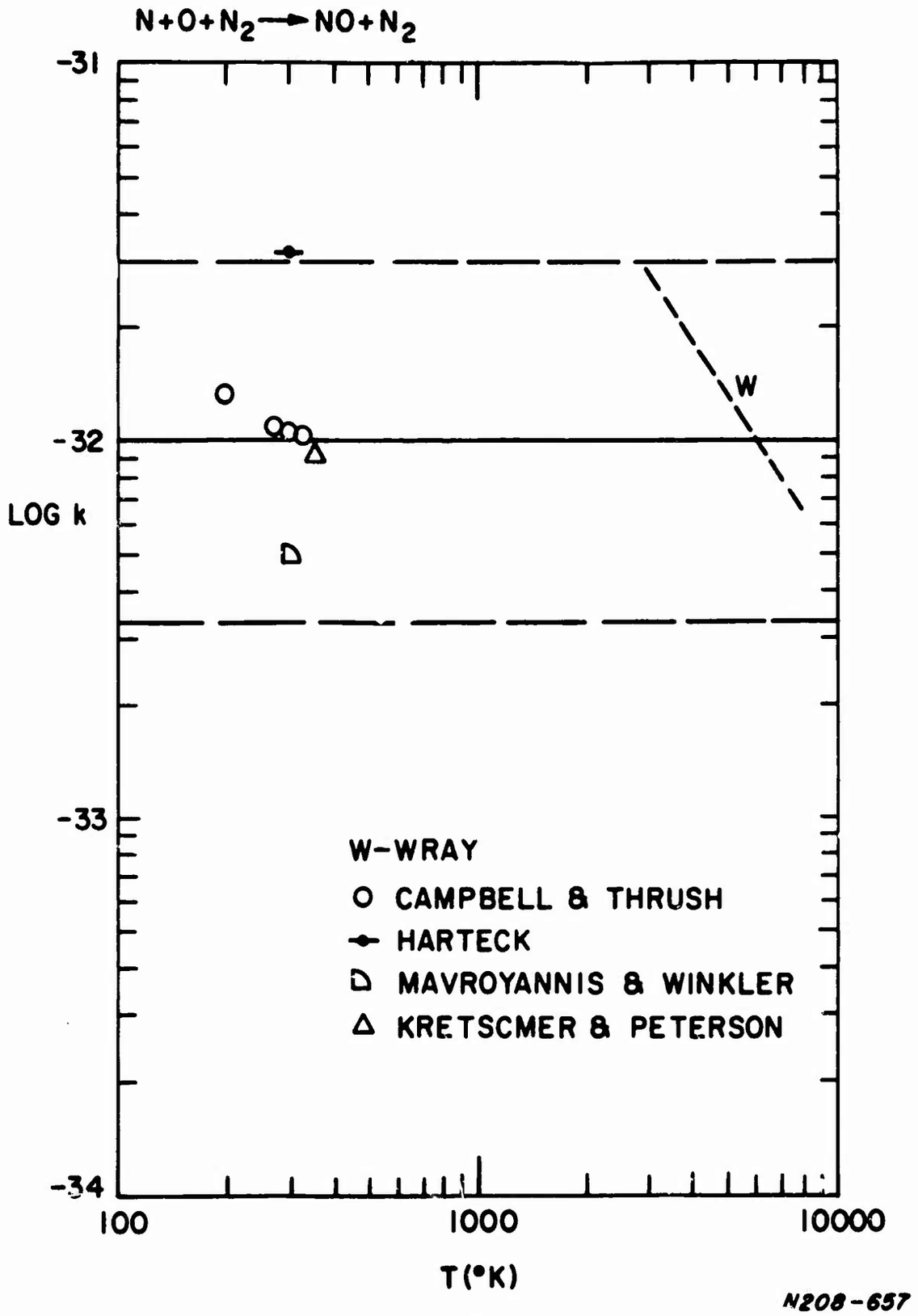

N+O+N2 → NO+N2
-31
-32
-33
-34
LOG k
W
W-WRAY
O CAMPBELL & THRUSH
HARTECK
MAVROYANNIS & WINKLER
KRETSCMER & PETERSON
100
1000
10000
T(°K)
N208-657

Figure 9

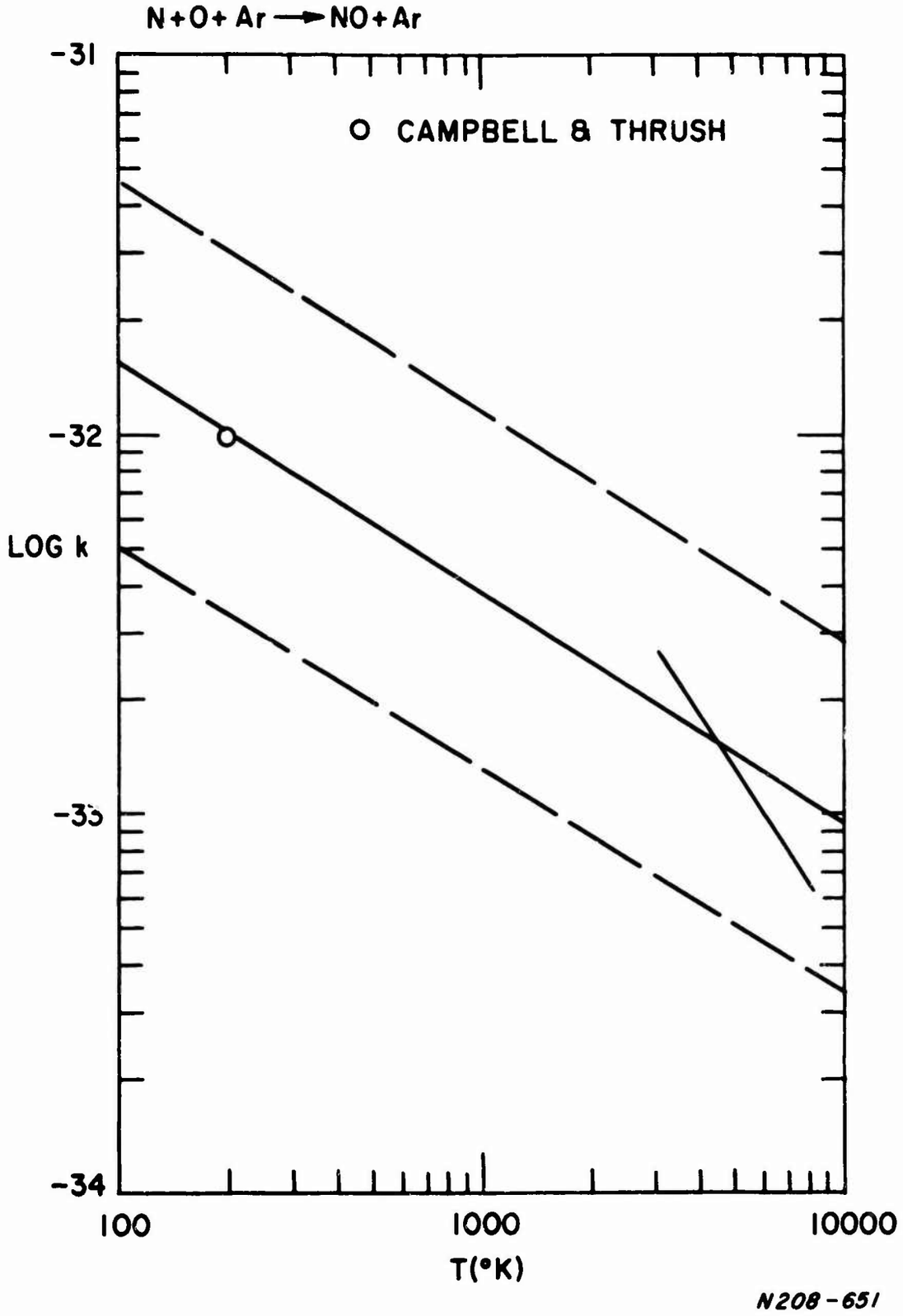

N+O+Ar → NO+Ar
-31
O CAMPBELL & THRUSH
-32
LOG k
-33
-34
100
1000
10000
T(°K)
N208-651

Figure 10

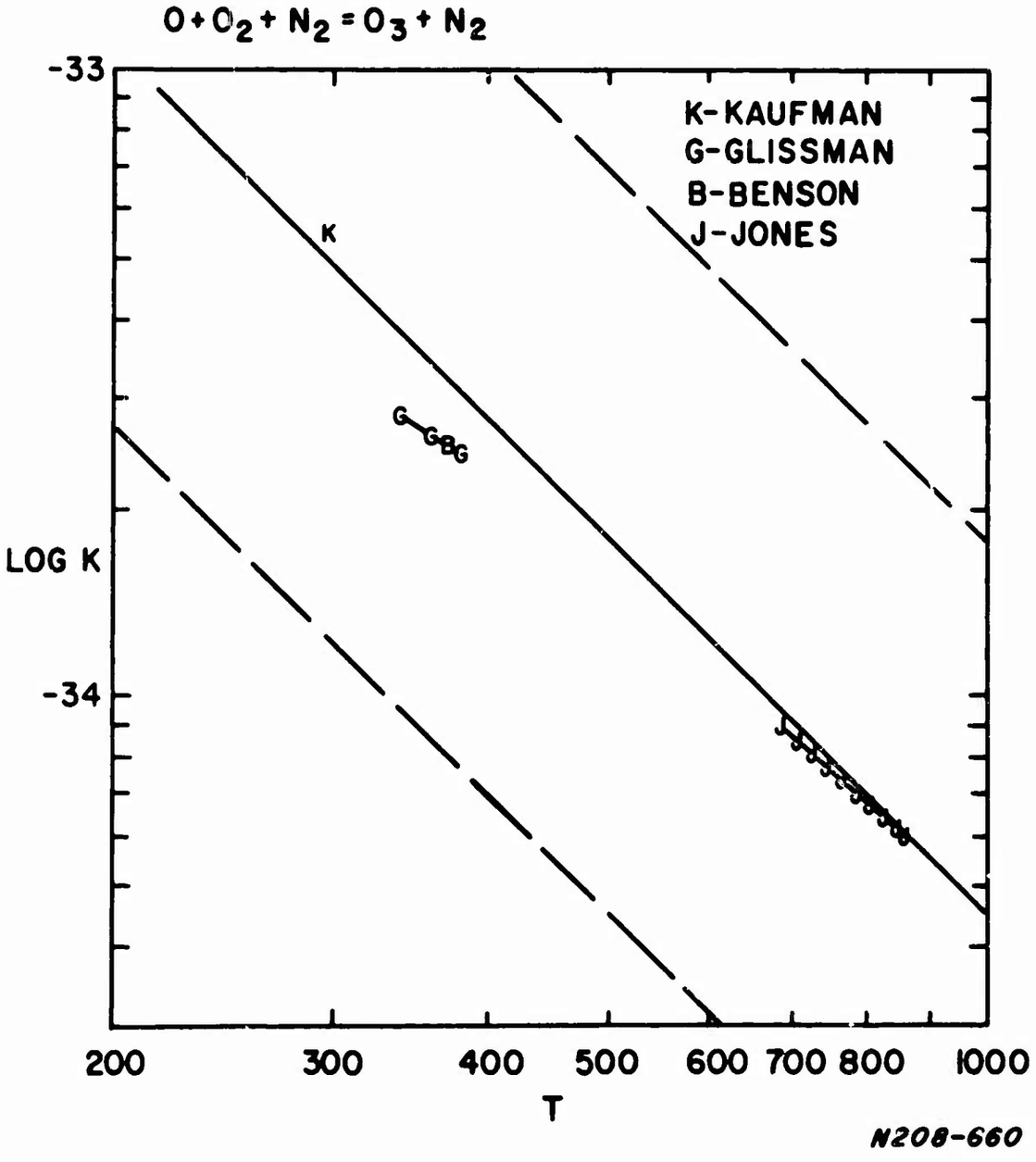

O + O2 + N2 = O3 + N2
-33
-34
LOG K
K-KAUFMAN
G-GLISSMAN
B-BENSON
J-JONES
K
G
G
B
G
200
300
400
500
600
700
800
1000
T
N208-660

Figure 11

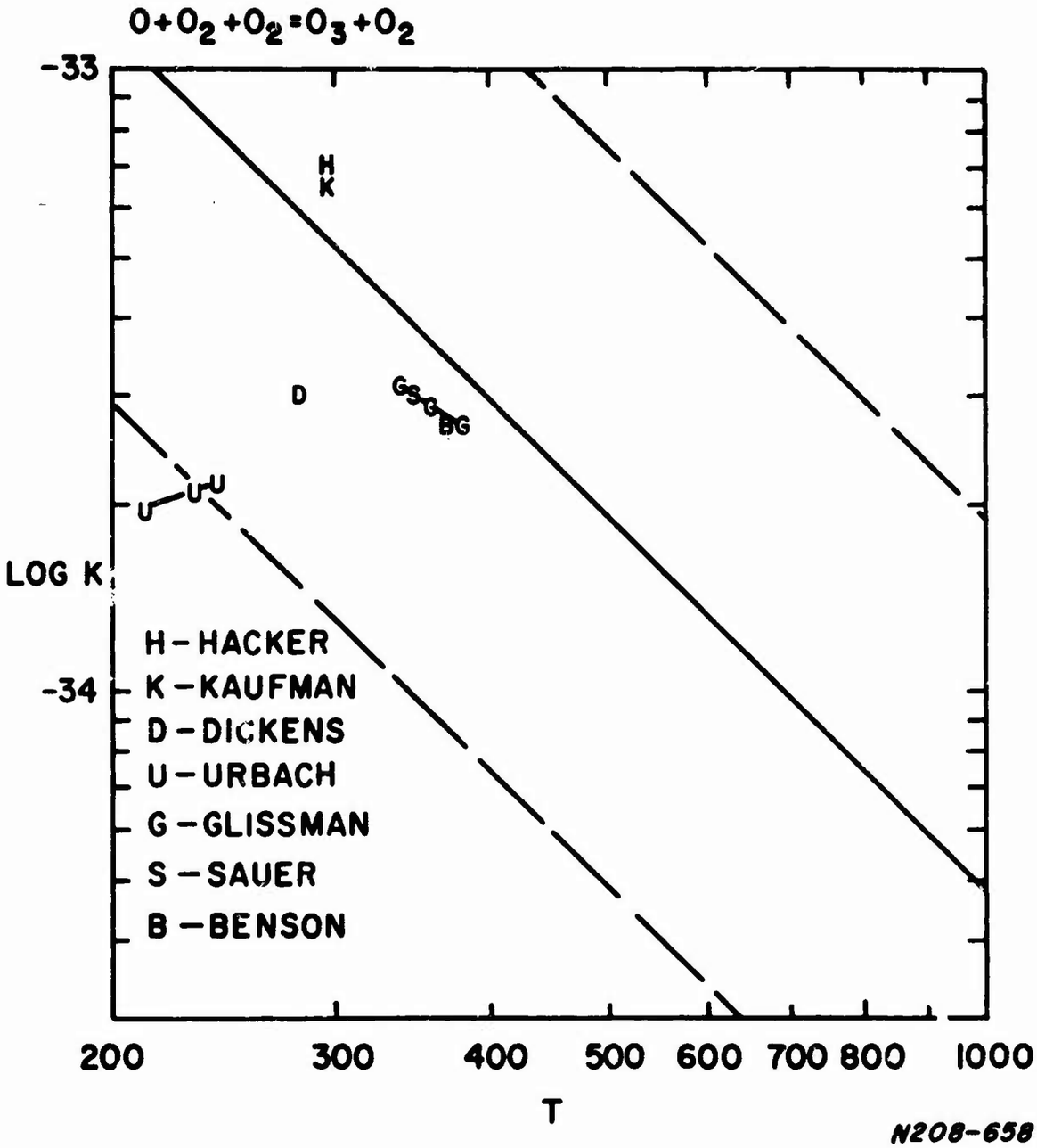

$O+O_2+O_2=O_3+O_2$
-33
-34
LOG K
H
K
D
G
S
G
BG
U
U
U
H - HACKER
K - KAUFMAN
D - DICKENS
U - URBACH
G - GLISSMAN
S - SAUER
B - BENSON
200
300
400
500
600
700
800
1000
T
N208-658

Figure 12

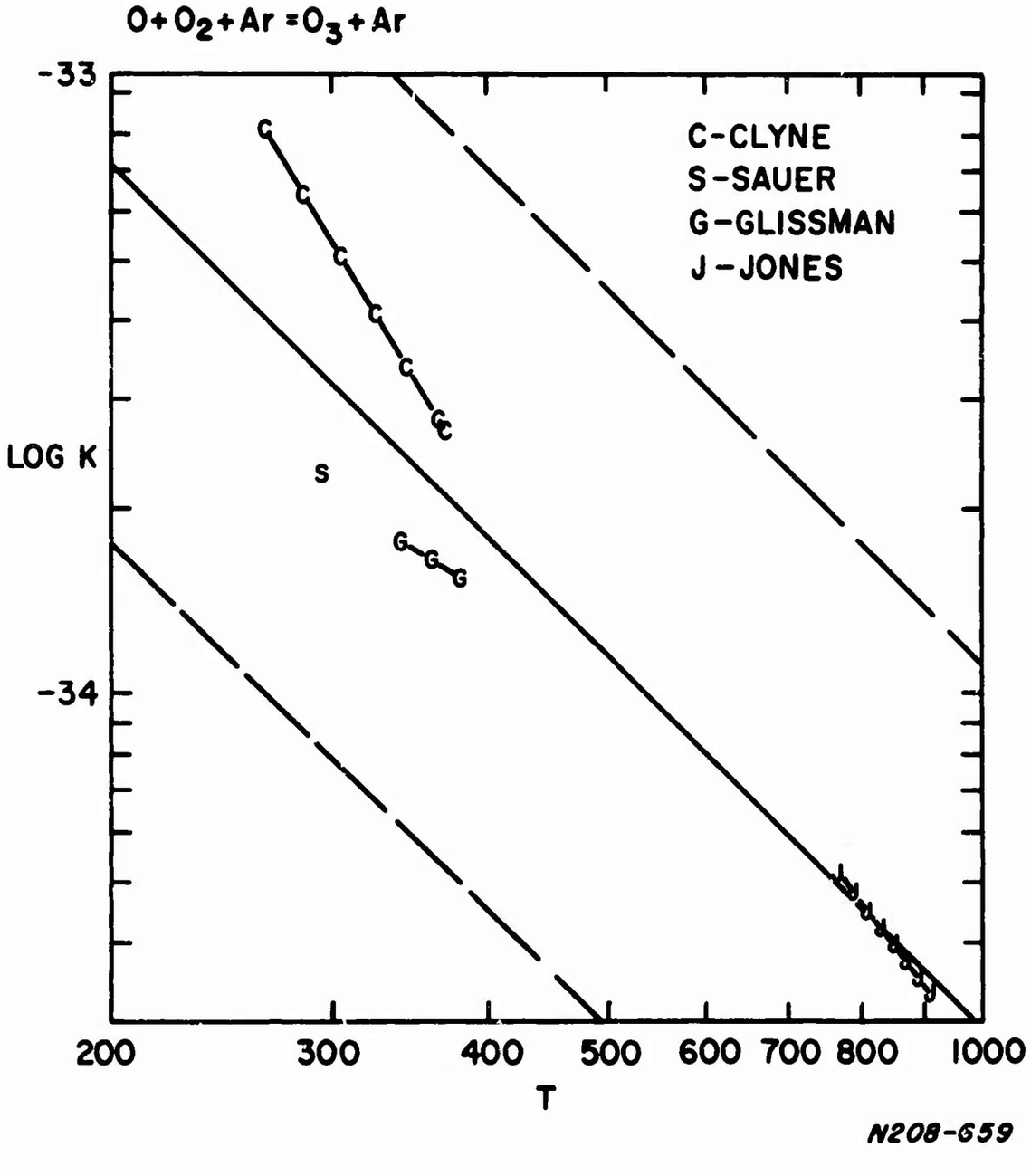

O+O2+Ar =O3+Ar
-33
-34
LOG K
C-CLYNE
S-SAUER
G-GLISSMAN
J-JONES
200
300
400
500
600
700
800
1000
T
N208-659

Figure 13

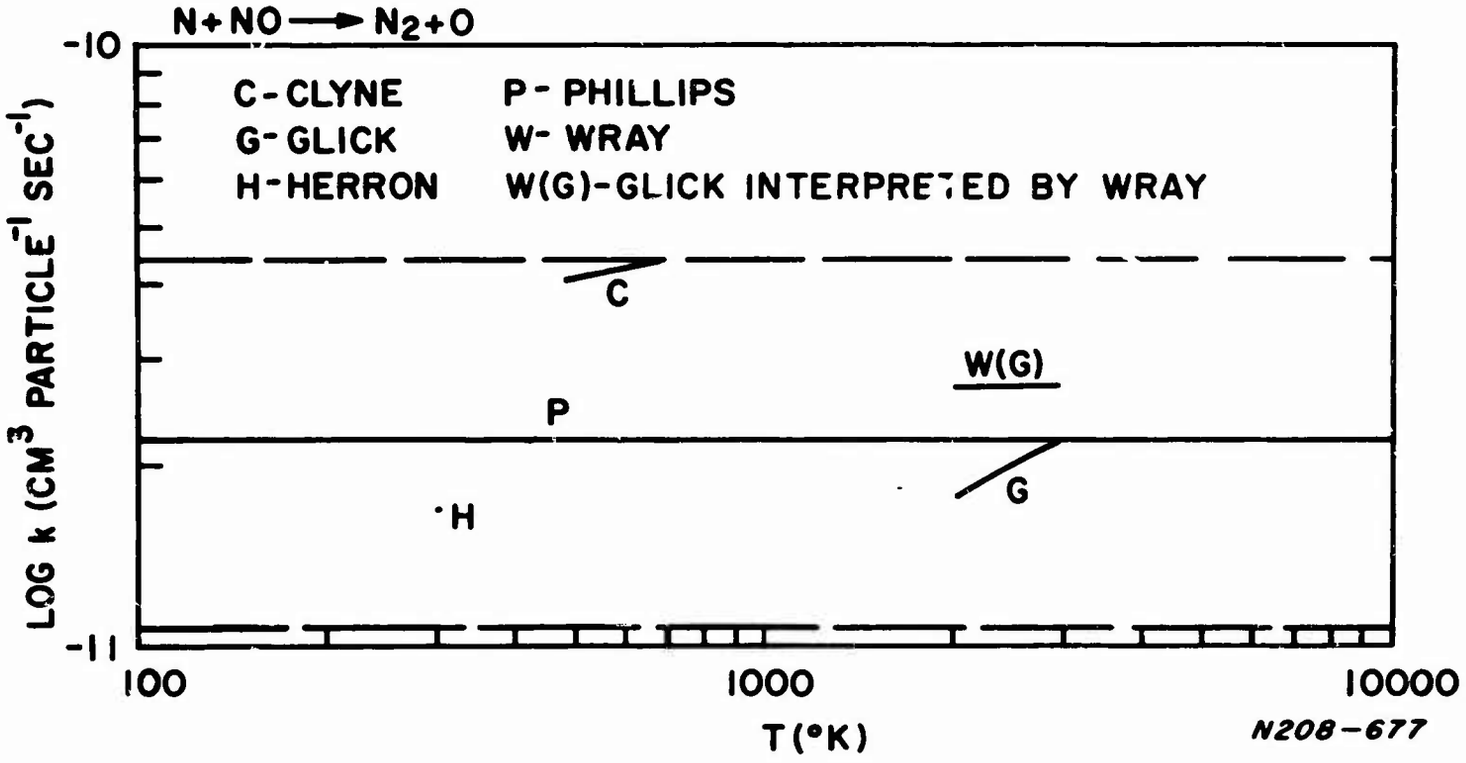

N+NO → N2+O
C - CLYNE
G - GLICK
H - HERRON
P - PHILLIPS
W - WRAY
W(G) - GLICK INTERPRETED BY WRAY
C
W(G)
P
G
H
-10
-11
LOG k (CM3 PARTICLE-1 SEC-1)
100
1000
10000
T(°K)
N208-677

Figure 14

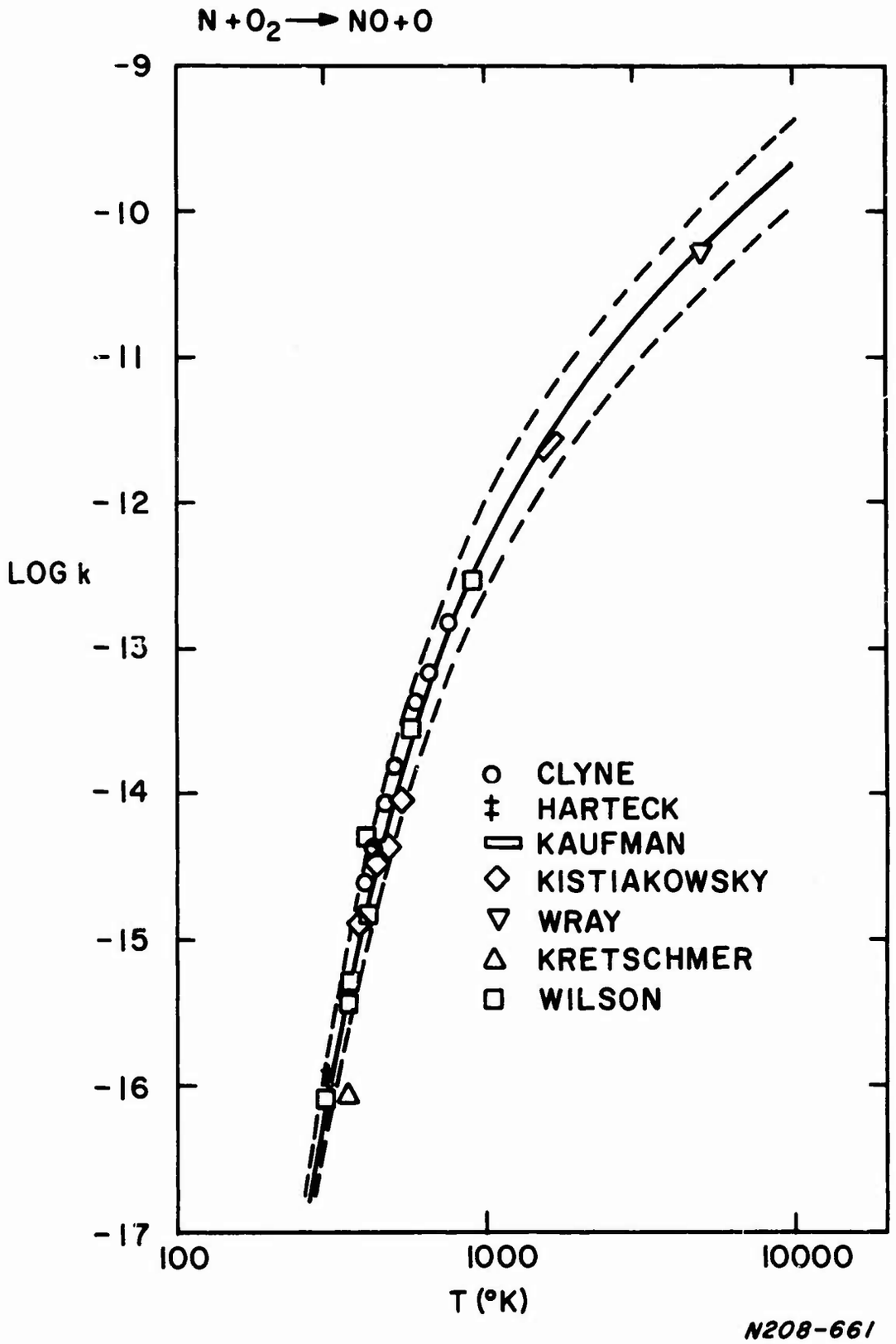

N + O2 → NO + O
-9
-10
-11
-12
-13
-14
-15
-16
-17
LOG k
100
1000
10000
T (°K)
CLYNE
HARTECK
KAUFMAN
KISTIAKOWSKY
WRAY
KRETSCHMER
WILSON
N208-661

Figure 15

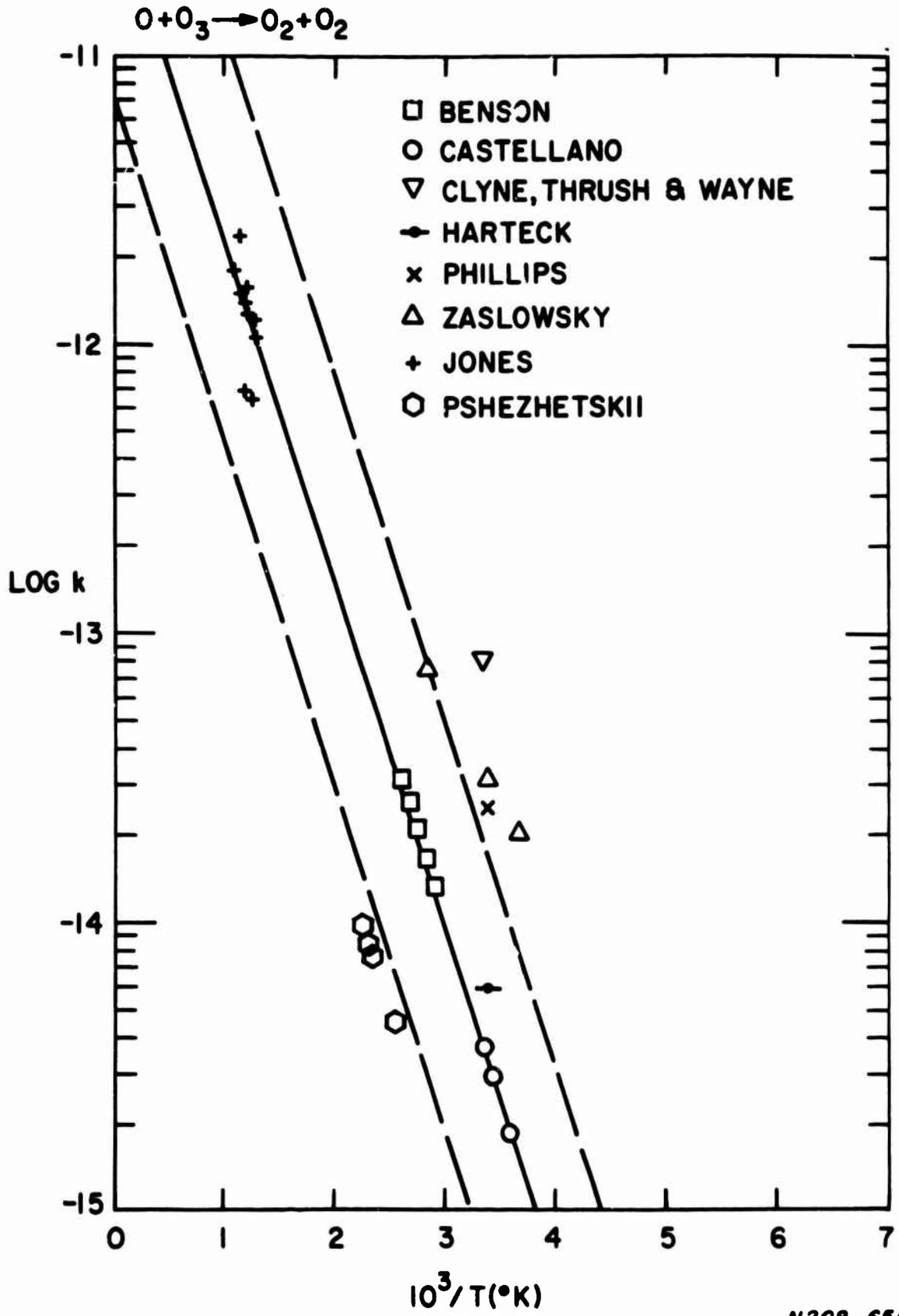

$O+O_3 \rightarrow O_2+O_2$
BENSON
CASTELLANO
CLYNE, THRUSH & WAYNE
HARTECK
PHILLIPS
ZASLOWSKY
JONES
PSHEZHETSKII
LOG k
-11
-12
-13
-14
-15
0
1
2
3
4
5
6
7
$10^3/T(°K)$
N208-656

Figure 16

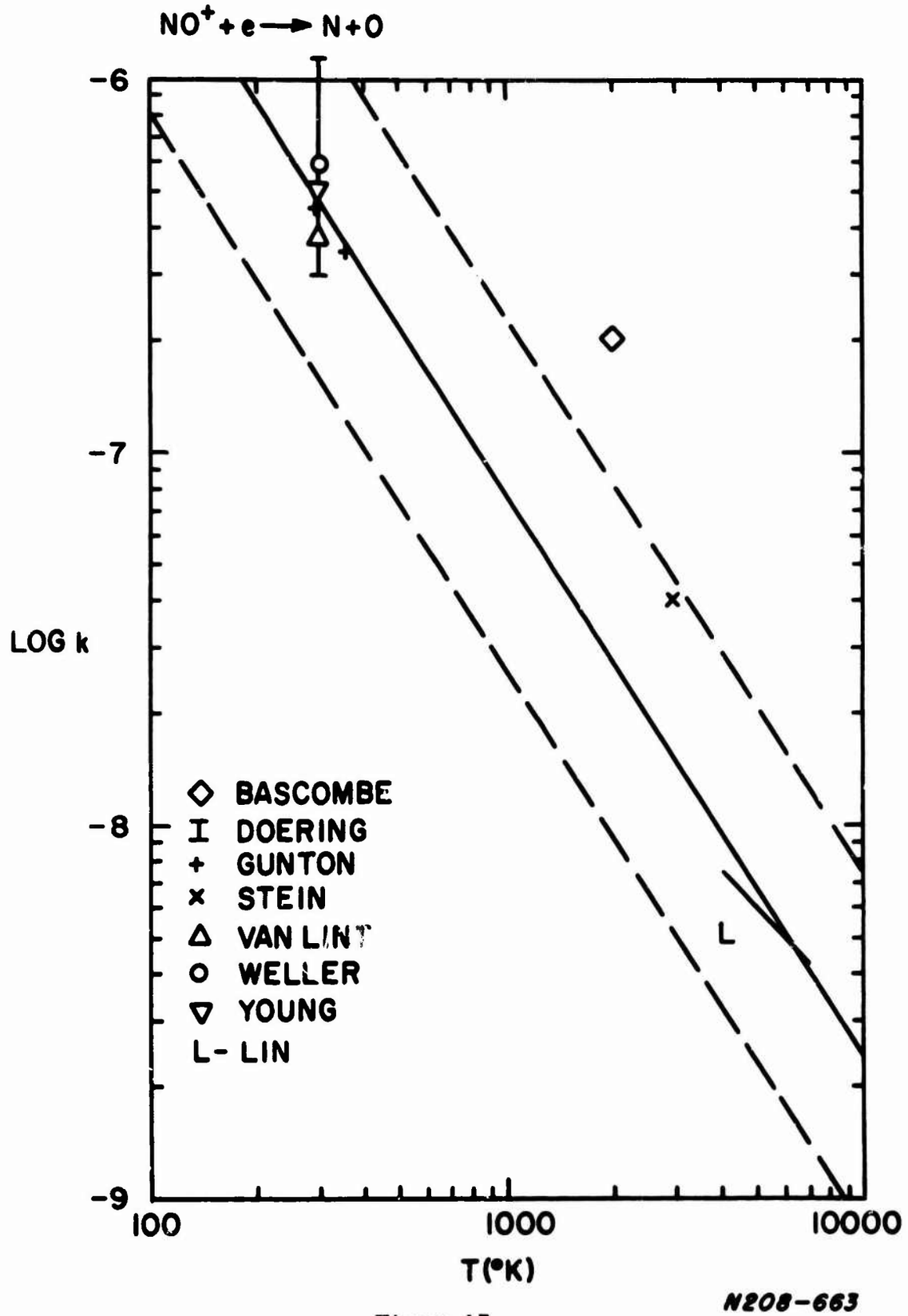

NO+ + e → N+O
-6
-7
-8
-9
LOG k
100
1000
10000
T(°K)
◇ BASCOMBE
I DOERING
+ GUNTON
× STEIN
△ VAN LINT
○ WELLER
▽ YOUNG
L- LIN
L
N208-663

Figure 17

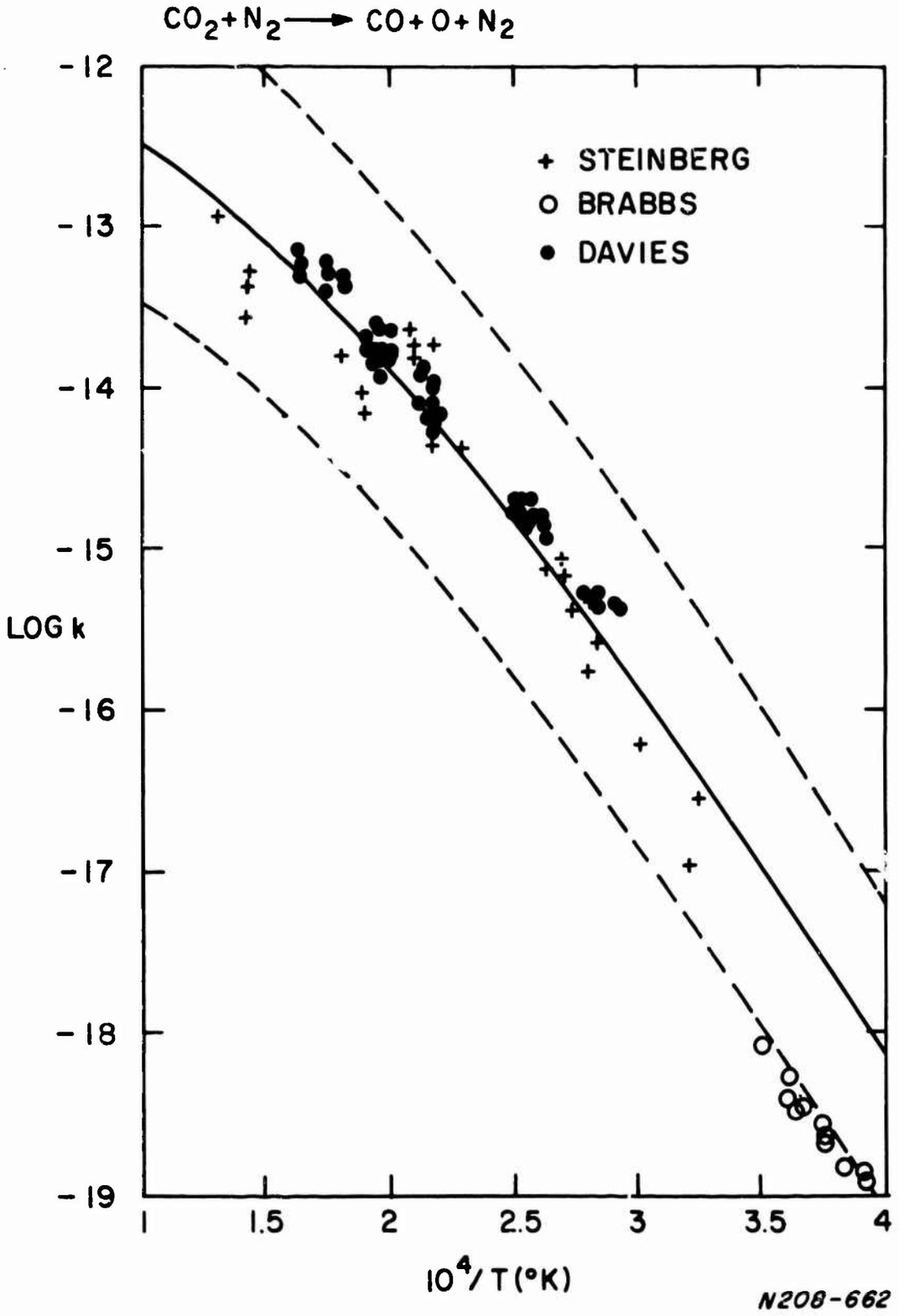

$CO_2 + N_2 \longrightarrow CO + O + N_2$
STEINBERG
BRABBS
DAVIES
LOG k
-12
-13
-14
-15
-16
-17
-18
-19
1
1.5
2
2.5
3
3.5
4
$10^4/T(°K)$
N208-662

Figure 18

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